Ab Initio XRPD Structure Determination of Metal Carbonyl Clusters: The Case of $[HgRu(CO)_4]_4$

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The crystal and molecular structure of the new $[HgRu(CO)_4]_4$ cluster has been determined exclusively from X-ray powder diffraction data from standard laboratory equipment and refined with a (modified) Rietveld procedure. The title compound crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.032(1)$ Å, $b = 18.293(2)$ Å, $c = 6.501(1)$ Å, $\beta = 111.81(2)°$, $V = 1438.9(4)$ Å^3, and $Z = 2$; the final refinement converged to R_p and R_{wp} values of 0.097 and 0.126, respectively, for 3351 data collected (Cu Kα) at room temperature in the 18–85° (2θ) range. $[HgRu(CO)_4]_4$ consists of a planar, centrosymmetric, eight-membered ring of alternating Hg and *cis*-$Ru(CO)_4$ units of idealized D_{4h} symmetry. XRPD is shown to be a powerful tool to obtain useful structural information on moderately complex organometallic systems, when single crystals cannot be grown, if all the available chemical knowledge is included in the refinement through constraints.

Introduction

X-ray powder diffraction (XRPD) has traditionally been the realm of materials scientists dealing with relatively simple and highly symmetric extended structures, and very little has been done in the field of organic and organometallic chemistry. Indeed, until very recently XRPD has mainly been applied to known molecular structures. Nowadays, the use of high-quality powder diffraction data (from synchrotron sources or neutron beams) and the development of many computational tools for powder diffractometry[1] have made *ab initio* determination of the unknown structures of small molecular or ionic systems possible, as beautifully demonstrated in the recent papers of Cernik *et al.*,[2] McCusker,[3] and Delaplane *et al.*[4] There is still a disparity between the complexity of structures that can be solved *ab initio* and those that can in principle be refined by Rietveld's method,[5] but Morris *et al.*,[6] using combined neutron and synchrotron X-ray powder diffraction, have recently determined, *ab initio*, the structure of $Ga_2(HPO_3)_3 \cdot 4H_2O$ (29 atoms in the asymmetric unit, 117 structural parameters), showing that complex structures can be determined with powder diffraction. Noteworthy is a 26-atom problem successfully tackled by Rudolf *et al.*,[7] who solved and refined the structure of $(AlPO_4)_3 \cdot (CH_3)_4NOH$ back in 1986 using a conventional source. Recently, the structural solution and refinement of the complex β-Ba_3AlF_9 phase[8] has raised the upper limit for conventional powder diffractometry up to 29 atoms in the asymmetric unit. Moreover, a limited number of crystal structures containing small organic fragments determined solely from powder diffraction data has been reported.[9]

To the best of our knowledge little[10] has been done on *molecular* organometallic compounds mostly because (i) their tendency to crystallize in the less symmetric space groups (often with large-size unit cells), (ii) the presence of weak intermolecular interactions (determining soft vibrational modes in the crystals, high thermal parameters, a rapid falloff of the scattering power with the θ angle, and often, large intrinsic peak widths), and (iii) the possibility of growing single crystals by many different simple techniques have kept structural chemists away from the field. Nevertheless, we have recently started a project about *ab initio* conventional XRPD on organometallics which fail to afford, for many reasons, single crystals of reasonable size; indeed in several cases the low solubility and/or the poor thermal stability hamper the use of most of the available methods of crystal growth, such as slow diffusion, gel permeation, evaporation techniques, and crystallization from the melt. A first achievement was the polymeric binary metal carbonyl $[Ru(CO)_4]_n$.[11] In this paper we present the *ab initio* crystal structure determination of the new highly insoluble $[HgRu(CO)_4]_4$ metal carbonyl cluster, i.e. the ruthenium analogue of the already known $[HgFe(CO)_4]_4$,[12] which was designed to demonstrate that even *laboratory* XRPD can afford useful *gross*

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[1] See for example: *Modern Powder Diffraction*; Reviews in Mineralogy 20; Bish, D. L., Post, J. E., Eds.; The Mineralogical Society of America: Washington, DC, 1990.

[2] Cernik, R. J.; Cheetham, A. K.; Prout, C. K.; Watkin, D. J.; Wilkinson, A. P.; Willis, B. T. M. *J. Appl. Crystallogr.* **1991,** *24,* 222.

[3] McCusker, L. B. *J. Appl. Crystallogr.* **1988,** *21,* 305.

[4] Delaplane, R. G.; David, W. I. F.; Ibberson, R. M.; Wilson, C. C. *Chem. Phys. Lett.* **1993,** *201,* 75.

[5] Rietveld, H. M. *J. Appl. Crystallogr.* **1969,** *2,* 65.

[6] Morris, R. E.; Harrison, W. T.; Nicol, J. M.; Wilkinson, A. P.; Cheetham, A. K. *Nature* **1992,** *359,* 519.

[7] Rudolf, P. R.; Saldarriaga-Molina, C.; Clearfield, A. *J. Phys. Chem.* **1986,** *90,* 6122.

[8] Le Bail, A. *J. Solid State Chem.* **1993,** *103,* 287.

[9] Berg, J. E.; Werner, P. E. *Z. Kristallogr.* **1977,** *145,* 310. Weiss, E.; Corbelin, S.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 650. Tremayne, M.; Lightfoot, P.; Mehta, M. A.; Bruce, P. G.; Harris, K. D. M.; Shankland, K.; Gilmore, C. J.; Bricogne, G. *J. Solid State Chem.* **1992,** *100,* 191. Williams, J. H.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1655. Lightfoot, P.; Tremayne, M.; Harris, K. D. M.; Bruce, P. G. *J. Chem. Soc., Chem. Commun.* **1992,** 1012.

[10] Lightfoot, P.; Glidewell, C.; Bruce, P. G. *J. Mater. Chem.* **1992,** *2,* 361.

[11] Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993,** 471.

[12] $[HgFe(CO)_4]_4$ has been known for a long time and was considered isomorphous with $[CdFe(CO)_4]_4$ (Takano, T.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1971,** *44,* 431); the structure of the latter was later determined by Ernst *et al.* (Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977,** *99,* 2090).

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stereochemical information on *complex structures*.[13] That is, the use of conventional X-ray tubes limits the accuracy and the precision of the refinements but still allows the formulations of good models for the packing and the atom–atom connectivity, when the spectra are accurately digitized and all the previous chemical knowledge is incorporated in the refinements by using constraints.

Experimental Section

Synthesis of $[HgRu(CO)_4]_4$. $[Ru_3(CO)_{12}]$ (200 mg) and mercury (1 g) were placed in a two-necked flask equipped with a reflux condenser and a gas inlet. The apparatus was purged with nitrogen, and THF (50 mL) was added. The mixture was refluxed while being vigorously stirred for 9 h, after which $[Ru_3(CO)_{12}]$ had completely disappeared (as evidenced by IR spectroscopy) and a black suspension was formed. This was filtered and washed with THF to give 220 mg of gray $[HgRu(CO)_4]_4$: ν_{CO} (Nujol) 2063 sh, 2053 s, 2024 m, 1999 s, 1989 sh, 1971 s, 1946 s (br), 1916 sh cm^{-1}; yield 57%. This IR spectrum closely resembles, in both its shape and peak positions, the one already reported for $[CdFe(CO)_4]_4$. Comparison of the IR spectra (KBr pellets) also excludes the identity of $[HgRu(CO)_4]_4$ as being the *yellow* compound prepared from $[HRu_3(CO)_{11}]^-$ and HgI_2, which has been proposed to be a polymeric form of $HgRu(CO)_4$.[14] The black solution (containing one or more unidentified cluster compounds) was refluxed for 15 h more, after which time a black precipitate was formed and no carbonyl compounds were present in solution. The IR of this insoluble material showed a very broad absorption at 1978 cm^{-1} with shoulders indicative of a complex, perhaps polymeric, structure. The powders proved, however, to be amorphous and were not further investigated. Only a trace amount of $[HgRu(CO)_4]_4$ was present in this sample; thus, the cluster observed in solution is not an intermediate of its synthesis.

X-ray Powder Diffraction of $[HgRu(CO)_4]_4$. The gray $[HgRu(CO)_4]_4$ powder was gently ground in an agate mortar and then cautiously deposited with the aid of a binder (5% collodion in amyl acetate) onto a Si wafer cut perpendicularly to the (511) direction (supplied by *The Gem Dugout*), minimizing the scattering from the substrate. The specimen was rotated at about 60 rpm around the scattering vector, to minimize preferred orientation effects. XRPD data were taken with Cu Kα radiation (λ = 1.5418 Å) on a Rigaku D/MAX-B horizontal scan powder diffractometer equipped with parallel Soller slits and a graphite monochromator in the diffracted beam, a Na(Tl)I scintillation counter, and pulse height amplifier (PHA) discrimination. Two different XRPD spectra were recorded, one enhancing angular resolution for the correct location of the peak positions to be used in the indexing procedure, the other maximizing the intensity and minimizing the preferred orientation, to be used for the structure solution and in the refinements. Data were collected (for the final run) in the 5–85° (2θ) range, in the θ–2θ mode and step scan with $\Delta 2\theta$ = 0.02° and t = 10 s. The generator was operated at 40 kV and 30 mA. Slits used: DS, 1.0°; AS, 1.0°; RS, 0.15°. Standard peak search methods were used for locating the diffraction maxima. In order to improve the precision of the derived values, profile fitting[15] of the first 13 peaks was performed, using a split Pearson VII function.[16]

Results and Discussion

Synthesis. Despite the fact that many compounds have been reported with the stoichiometry $[B_nMFe(CO)_4]_m$ (B = nitrogen base; n = 0–3; M = Zn, Cd, Hg, Pb) or $R_2(B_n)M'Fe(CO)_4$ (R = alkyl; M′ = Si, Ge, Sn, Pb; n = 0, 1),[17] no ruthenium analogue has been reported up to now, with the notable exception of the poorly characterized $[HgRu(CO)_4]_n$ polymer.[14] This is due, at least in part, to the fact that the syntheses of all the aforementioned compounds use $Fe(CO)_5$ as a starting material. Even though $Ru(CO)_5$ is a known molecule, it is far less stable than its iron analogue and rapidly yields $[Ru_3(CO)_{12}]$ unless kept in the dark at very low temperature.[18] Thus, extension of this iron chemistry to ruthenium is not straightforward. $[HgFe(CO)_4]_4$ is synthesized by reaction of $Fe(CO)_5$ with mercury sulfate in the presence of water, but a corresponding synthesis is not viable in our case. We succeeded, however, in obtaining $[HgRu(CO)_4]_4$ from $[Ru_3(CO)_{12}]$ with metallic mercury in refluxing THF in a good chemical yield. Although the tetrameric compound was the only one obtained in pure form, other compounds were likely candidates as products, including a polymeric $[HgRu(CO)_4]_n$, containing chains of Hg–Ru units, built either from *cis*-C_{2v}[14] or *trans*-D_{4h} Hg–$Ru(CO)_4$–Hg links. To try to force the reaction in this direction, we attempted to react mercury with polymeric $[Ru(CO)_4]_n$.[11] No reaction occurred, however, even on lengthening the time scale or by increasing the reaction temperature by working in refluxing toluene. The tetrameric Hg derivatives are highly insoluble in all common solvents even in the presence of 2,2′-bipyridyl, which, acting as a deoligomerizing agent, allowed the (re)crystallization of $[CdFe(CO)_4]_4$ from actone;[12] thus, all physicochemical information must be extracted from powder samples only.

X-ray Analysis. Unit cell dimensions were obtained from the trial and error indexing program TREOR;[19] a reasonable agreement for all peaks was found within the monoclinic system, with a = 13.042 Å, b = 18.324 Å, c = 6.504 Å, β = 111.82°, $M(20)$ = 25, and $F(20)$ = 51 (0.008, 51); the space group $P2_1/n$ (No. 14) was chosen from systematic absences and subsequently confirmed by satisfactory refinement.[20] Comparison of the derived lattice parameters showed that, fortunately, the few related species with a (supposed) similar molecular structure, $[CdFe(CO)_4]_4 \cdot 2C_3H_6O$,[12] $[AgCo(CO)_4]_4$,[21] and $[CuCo(CO)_4]_4$,[22] were not isomorphous. Hence, $[HgRu(CO)_4]_4$ is an ideal example of a compound with (supposedly) known molecular topology but unknown crystal structure

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[13] Early work with laboratory X-ray data has mainly concerned classical inorganic compounds. For instance, see: Rudolf, P.; Clearfield, A. *Acta Crystallogr.* **1985**, *B41*, 418. LeBail, A. *Powder Diffraction Meeting*, Toulouse, France, 1990; Book of Abstracts, p 99.

[14] Rosenberg, E.; Ryckman, D.; Hsu, I.-N.; Gellert, R. W. *Inorg. Chem.* **1986**, *25*, 194.

[15] Toraya, H.; Yoshimura, M.; Somiya, A. *J. Appl. Crystallogr.* **1983**, *16*, 653.

[16] Hall, M. M.; Veeraraghavan, V. G.; Rubin, H.; Westdahl, M. *J. Appl. Crystallogr.* **1977**, *10*, 66.

[17] Ernst, R. D.; Marks, T. J. *Inorg. Chem.* **1978**, *17*, 1477 and references therein.

[18] Calderazzo, F.; L'Eplattenier, F. *Inorg. Chem.* **1967**, *6*, 1220.

[19] Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367. One of the major tasks to be accomplished in *ab initio* structural determinations from XRPD data is the formulation of the correct lattice parameters. The intrinsic or accidental overlap of several reflections makes this step very difficult, and the ultimate check for the correctness of any lattice metric based on powder diffraction data only is the satisfactory refinement of the structure. The quality of the pattern, i.e. the absolute error in the 2θ location of the peaks and the amount of instrumental aberrations (zero angle setting, specimen displacement error, etc.), can limit the approximate maximum volume of indexable cells, which, for typical laboratory equipment, must be lower than e.g. 2000 Å^3.

[20] The indices of all intense peaks seemed to indicate the presence of a *body-centered* lattice; however, the presence of a weak, but clearly measured, peak at about 12° 2θ (*120*) suggested that a *primitive* lattice should be taken instead. That is, a very small, but detectable, distortion from the idealized $I2/m$ space group is present, with the $P2_1/n$ subgroup best representing the true situation. Accordingly, the final refined coordinates are close, but not coincident, to those expected for a body-centered lattice. As a consequence, the rigid-body x and z rotation values (90 and 0°, respectively, in the $I2/m$ space group) only slightly deviate from these values in $P2_1/n$ (see Table I).

[21] Klufers, P. *Z. Kristallogr.* **1984**, *166*, 143.

[22] Klufers, P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 307.

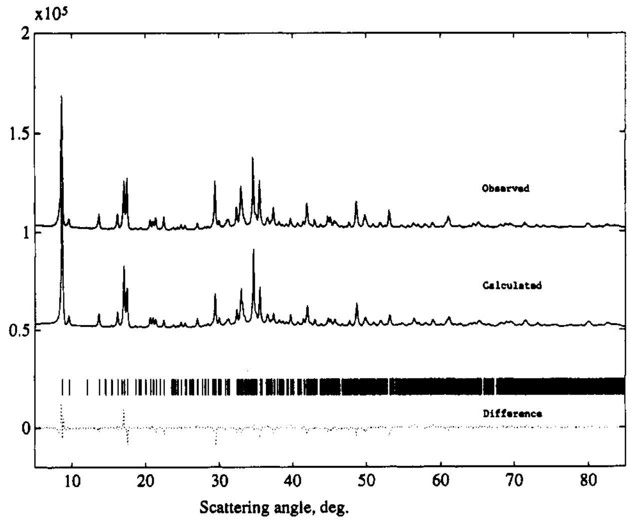

Figure 1. Plot of the observed (top) and calculated (middle) XRPD spectra of $[HgRu(CO)_4]_4$. The difference plot is also shown (bottom, dotted line). Reflection positions are marked by vertical bars.

Table I. Crystal Data and Refined Parameters

Crystal Data	
compd	$[HgRu(CO)_4]_4$
formula	$C_{16}O_{16}Hg_4Ru_4$
fw	1654.81
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
α, Å	13.032(1)
b, Å	18.293(2)
c, Å	6.501(1)
β, deg	111.81 (2)
vol, Å^3	1438.9(4)
Z	2
D_{calc}, g cm^{-3}	3.819
μ(Cu Kα), cm^{-1}	577.5
F(000)	1440
U	0.594(6)
V	−0.282(2)
W	0.0697(6)
asymmetry factor P	0.10(5)
preferred orientation G(110)	0.910(8)
B(Ru), Å^2	1.86(3)
B(Hg), Å^2	1.40(9)
B(C) = B(O), Å^2	2.6(4)
Generalized Coordinates	
rot. x, rad	1.527(4)
rot. y, rad	−0.548(1)
rot. z, rad	0.030(2)
origin–Ru, Å	3.782(2)
origin–Hg, Å	2.473(3)
origin–Ru–C_{eq}, deg	128.682(5)
origin–Ru–C_{ax}, deg	83.504(3)

Table II. Fractional Atomic Coordinates for $[HgRu(CO)_4]_4$ (Esd's in Parentheses)

atom	x/a	y/b	z/c
Ru1	0.0019(10)	−0.2067(2)	0.0231(17)
Hg1	0.1245(5)	−0.0934(4)	0.2434(12)
Ru2	0.2667(3)	0.0051(4)	0.5022(7)
Hg2	0.1237(13)	0.0989(8)	0.2237(20)
C1	−0.1031(13)	−0.2742(2)	−0.1685(22)
O1	−0.1649(15)	−0.3140(3)	−0.2813(25)
C2	0.1082(13)	−0.2702(2)	0.2294(22)
O2	0.1708(15)	−0.3076(3)	0.3508(25)
C3	−0.0805(10)	−0.1918(5)	0.2107(16)
O3	0.1290(10)	−0.1831(7)	0.3211(16)
C4	0.0841(10)	−0.1978(5)	−0.1671(16)
O4	0.1325(10)	−0.1925(7)	−0.2790(17)
C5	0.3520(5)	−0.0751(6)	0.6706(10)
O5	0.4023(7)	−0.1224(6)	0.7697(14)
C6	0.3505(6)	0.0886(5)	0.6523(10)
O6	0.3998(8)	0.1378(6)	0.7406(14)
C7	0.1691(4)	0.0078(5)	0.6622(4)
O7	0.1116(5)	0.0094(7)	0.7564(4)
C8	0.3337(2)	0.0018(7)	0.2844(9)
O8	0.3731(2)	−0.0001(9)	0.1563(11)

which may be used to demonstrate the performance of a two-step method,[23] consisting of a whole-pattern profile-fitting technique[24] in conjunction with a real-space scavenger (of a known model) specifically developed for powder data.[25] Therefore, the integrated intensities were extracted with the aid of Toraya's program[24] and used to determine scale and average thermal factors from a Wilson plot. Using only the intensity data in the 5–40° (2θ) range (corresponding to 132 space-group-allowed reflections and 43 observations), and a Hg_4Ru_4 fragment of idealized D_{4h} symmetry, P-RISCON[25] succeeded in determining the location and orientation of the octametal cluster in the unit cell (for the best solution, an R_w value of 0.36 was obtained). Later on, direct methods[26] also resulted in the correct solution, showing the viability of ab initio XRPD analysis even in the absence of a structural model. The structure was refined with the program PREFIN,[27] locally modified for accepting generalized (geometrical) constraints using the Z-matrix formalism. Atomic scattering factors were taken from ref 28. The final model was assumed to possess isotropic thermal factors, linear carbonyl groups, and idealized D_{4h} symmetry. In the final refinement (18–85° range), the profile agreement factors R_p and R_{wp} were 0.097 and 0.126, respectively, and R_{Bragg} = 0.092. A parallel refinement in the $I2/m$ space group[20] gave slightly higher agreement factors (R_p = 0.101 and R_{wp} = 0.131). Figure 1 shows the plot of the observed and calculated profiles. Table I contains the summary of crystal data and list of the refined parameters, while derived fractional atomic coordinates are collected in Table II. Relevant distances and angles are reported in the caption for Figure 2.

Crystal and Molecular Structure of $[HgRu(CO)_4]_4$. $[HgRu(CO)_4]_4$ consists of a planar, centrosymmetric, eight-membered ring of alternating Hg and *cis*-$Ru(CO)_4$ units of idealized D_{4h} symmetry[29] and is confirmed to be isostructural (but not isomorphous!) with $[CdFe(CO)_4]_4$.[12] An ORTEP drawing of the molecule is shown in Figure 2. The two aforementioned derivatives differ, however, in the disposition of the Hg(Cd) atoms: four slightly attractive Hg⋯Hg long-range interactions favor the shrink-

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(23) Jansen, E.; Schäfer, E.; Will, G. *J. Appl. Crystallogr.* **1988**, *21*, 228.

(24) Toraya, H. *J. Appl. Crystallogr.* **1986**, *19*, 440.

(25) P-RISCON (Masciocchi, N.; Bianchi, R.; Cairati, P.; Pilati, T.; Sironi, A. *J. Appl. Crystallogr.*, submitted for publication), a locally modified version of RISCON (Bianchi, R.; Gramaccioli, C. M.; Pilati, T.; Simonetta, M. *Acta Crystallogr.* **1981**, *A37*, 65), originally developed for single-crystal data only, is capable of finding the location and orientation in the unit cell of one or more fragments of known geometry, provided that lattice parameters, space group, and a set of integrated intensities, for single peaks and/or *overlapped* multiplets, are supplied.

(26) SIRPOW: Cascarano, G.; Favia, L.; Giacovazzo, C. *J. Appl. Crystallogr.* **1992**, *25*, 310.

(27) PREFIN: Immirzi, A. *Acta Crystallogr.* **1978**, *A34*, S348; **1980**, *B36*, 2378.

(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

(29) Attempts to refine less symmetric models, down to the crystallographically imposed C_i symmetry, afforded slightly lower agreement factors, but also an unreasonable spread of chemically equivalent structural parameters. The presence of several *instrumental* sources of errors (preferred orientation effects, peak shape, etc.), as well as of extreme peak overlap at high diffraction angles (see Figure 1), therefore limits the accuracy attainable with the state-of-the-art techniques.

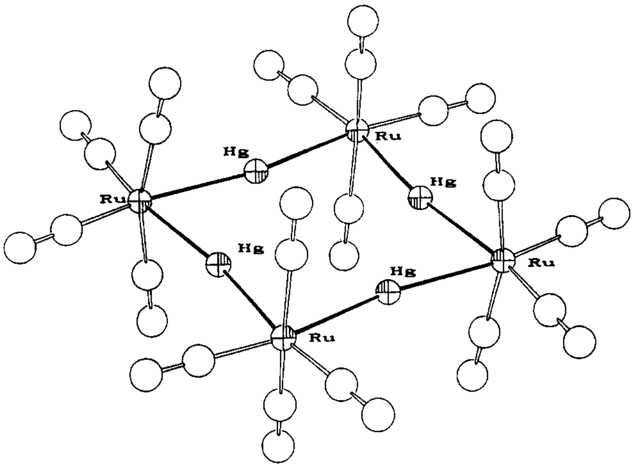

Figure 2. ORTEP drawing of $[HgRu(CO)_4]_4$. Relevant bonding parameters are as follows: Ru–Hg = 2.68(1) Å, Hg···Hg = 3.53(2) Å, Ru–C = 1.92 Å, C–O = 1.13 Å, Ru–Hg–Ru = 171.6(4)°, Hg–Ru–Hg = 82.0(4)°, C_{eq}–Ru–C_{eq} = 102.6(3)°, C_{ax}–Ru–C_{ax} = 167.0(4)°.

age of the Hg_4 fragment in $[HgRu(CO)_4]_4$; in contrast, two clathrate acetone molecules interacting with two Cd atoms determine a diamond distortion of the Cd_4 fragment, reducing the idealized symmetry of $[CdFe(CO)_4]_4$ to D_{2h}. The only *cis*-$Ru(CO)_4Hg_2$ fragment reported in the literature belongs to the *cis*-$Ru(CO)_4[HgRu_3(CO)_9(\mu_3\text{-}C_2\text{-}t\text{-}Bu)]_2$ molecule[14] and has highly comparable Ru–Hg (2.657 *vs* 2.68 Å) and Hg···Hg (3.55 *vs* 3.53 Å) interactions.

The crystal packing for $[HgRu(CO)_4]_4$, depicted in Figure 3, shows a pseudo-body-centered lattice, in agreement with previous considerations on the intensity distribution ($h + k + l = 2n + 1$ weak).[20] From the shortest intermolecular contacts (*all* C···O and O···O distances are above 3.0 Å), it is easily seen that the packing of the molecules is chemically sound, indirectly confirming the correctness of the proposed structural model. In addition, volume considerations exclude the presence in the crystal lattice of clathrated solvent molecules as in $[CdFe(CO)_4]_4{\cdot}2C_3H_6O$;[12] in fact, the volume difference between the Cd and Hg phases (1714 − 1439 = 275 Å^3) accounts, in accord with the Kempster–Lipson rule[30] (i.e. ca. 18 Å^3 per non-hydrogen main-group atom), "exactly" for the four acetone molecules found in the unit cell of the former.[31]

Despite the fact that many geometrical details are lost in the aforementioned analysis (for instance, by imposing idealized D_{4h} symmetry on the whole molecule), the results from XRPD data can be confidently used to investigate the packing modes of organic[32] and organometallic[33] molecules. As a matter of fact, the "arbitrary" idealization of the molecular model, often necessary when dealing with powder diffraction data, affects only slightly the packing analysis. Indeed, similar idealizations are commonly performed in all the packing analyses of organic molecules, because the *correct* locations of the "packing-sensitive" hydrogen atoms must be (re)determined even when dealing with the best set of single-crystal *X-ray* diffraction data.

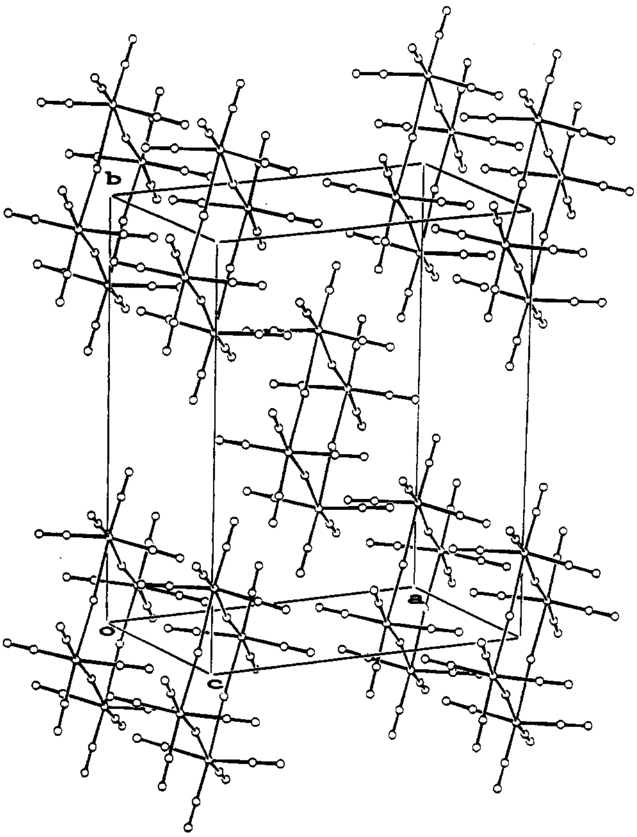

Figure 3. Crystal packing for $[HgRu(CO)_4]_4$.

Conclusions

These results confirm that conventional XRPD diffractometry is a powerful tool in the structural chemist's hands for obtaining *otherwise inaccessible* structural information on moderately complex organometallic systems (in the present case, 20 atoms in the asymmetric unit). The number of structural parameters which can be confidently refined is, however, limited by the intrinsic low resolution of the laboratory equipment. All the available chemical knowledge should therefore be included in the solution and refinement processes, by imposing geometrical constraints on the refined model, particularly when light atoms are involved (in the present case, 15 structural parameters only were refined).

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Supplementary Material Available: Full lists of positional and thermal parameters, bond distances and angles, and interatomic and intermolecular contacts (11 pages). Ordering information is given on any current masthead page.

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(30) Kempster, C. J. E.; Lipson, H. *Acta Crystallogr.* **1972**, *B28*, 3674.

(31) The aforementioned volume considerations are even stronger than the information obtainable from difference Fourier maps, which, besides not being available if PREFIN is used, can miss the presence of other atoms in the structure if noisy data (as high-angle intensities from XRPD are likely to be) are used.

(32) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.

(33) See for example: Braga, D.; Grepioni, F. *Organometallics* **1991**, *10*, 1254.