The contribution of powder diffraction methods to structural co-ordination chemistry

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X-Ray powder diffraction (PD) has been widely used in the past as a standard technique for quali- and quanti-tative phase analysis.[1] This is still the main field of application of the method, since its non-destructive nature raised it to a routine tool for quality control (of ores, metals, alloys, ceramics, high-tech materials, drugs and other commodities) in industrial processes. In addition, when the shape, width and position of the Bragg reflections began to be analysed in detail, the new field of microstructural analysis emerged,[2] and became an important method for material characterisation, probing strain, stress, texture, defects and stacking faults in a large variety of structures. Less well known applications of PD can also be found in pharmaceutical,[3] medical,[4] artistic[5] and forensic[6] sciences.

In the late 1970's, with the automation of diffractometers and the availability of large-scale facilities, a wide group of solid-state chemists, mineralogists and physicists stopped considering this technique as a complementary method for material characterisation and understood its inherent power. It was then clear that the structural information contained in a powder diffraction pattern could be retrieved by the simultaneous use of digitised data and by the development of numerical methods and algorithms for data analysis. This was the time of the boom of the Rietveld method,[7,8] which, relying on a predetermined model, was widely and successfully used for the characterisation of materials whose structures were mostly related to archetypal structures or their simple combinations.

Although an early successful structure determination from conventional data has been reported in 1977[9] (not to mention the work of Zachariasen and Ellinger[10] on β-Pu), it was certainly the pioneering work of Parrish and Hart[11] and Hastings *et al.*[12] (who built diffraction equipment, for synchrotron radiation, capable of reaching the ultimate resolution of 0.05° or less) which increased the confidence in the retrieval of structural information from PD patterns. It was then beautifully demonstrated that the *ab initio* structure solution of inorganic and organic molecules of moderate complexity (less than 20 non-H atoms in the asymmetric unit) could become a powerful, although expensive, tool affording atomic resolution.[13] Following these advances, conventional X-ray equipment was also progressively improved, thus opening the field to a much wider community than synchrotrons could ever accommodate. Paralleling the development of the hardware, in the early 1990's, a number of computational tools, specifically developed for powder diffraction methods, became available; they include, by now, more than one hundred programs tackling all steps from single peak location up to graphics and tabular presentation of the results;[14] a series of integrated systems, similar to those available for single crystal-data, is presently under development.[15]

Hereafter we shall call (in a purely nominal way) any structure determination which is not based on isomorphous or isotypic character of previously known crystal phases *ab initio* structure solution; this *formal* definition makes much sense in the realm of the powder diffraction methods, since for several decades, the use of the Rietveld method has *not* been associated with the many difficult steps described below. Despite the availability of the method, only a few groups are actively using *ab initio* PD; their fields of interest (mainly oxides,[16] fluorides,[17] nitrates,[18] silicates,[19] phosphates and phosphonates,[20] while less attention has been given to organic[21] and organometallic[22] compounds) have been strongly influenced by the personal track of their careers.

In the last five years, we have been active in this field with the goal of developing a general procedure for the characterisation of moderately complex co-ordination and organometallic compounds. In this paper we will focus mainly on our efforts in retrieving valuable structural information from rather complex PD patterns, showing the viability of the PD method even when unsophisticated, widely available (but well conditioned) laboratory equipment is employed. Note that, *molecular compounds*, mostly because of their tendency to crystallise in the less symmetric space groups (often with large unit cells) and of the presence of weak intermolecular interactions (leading to soft vibrational modes, high thermal parameters, rapid fall-off of the scattering power with the θ angle and, often, large intrinsic peak widths), are apparently less suited to PD experiments than *ionic compounds*. However, in the case of *co-ordination compounds* the presence of a few 'heavy' atoms simplifies the structure solution process, while that of conformationally rigid ligands may simplify structure refinements. In the authors' experience, the upper size limit for the volume of the asymmetric unit, which is mainly determined by the difficulties in indexing the powder spectrum, can be set to *ca.* 800 Å^3 (*i.e. ca.* 40 independent non-hydrogen atoms). Obviously, this rather optimistic limit can be reached only in the presence of well diffracting, *monophasic* samples obtainable in reasonable quantities (*ca.* 50 mg, smaller amounts can be used at the price of sample transparency effects which can be, in principle, analytically corrected). Note, however, that a recent structure determination of a *biphasic* mixture of two polymorphs of cyclopentadienylrubidium was performed on a single XRPD pattern, coupling the enhanced features of synchrotron radiation and a fortunate occurrence of a bimodal distribution of peak widths.[22b]

This contribution complements a number of recently published reviews disclosing the power of modern powder diffraction[23] to chemists working in other fields with similar tools.[20,24]

Radiation Choice and Efficiency

As far as structure solution is concerned, X-rays are clearly superior to neutrons (N, the phase problem being solved by a smaller set of atoms) and, because of the extraordinary level of angular resolution, tuneability (allowing a multiwavelength approach to structure solution) and intensity of synchrotron sources (S), these are superior to other more conventional

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equipment (X). Therefore, neutron diffraction has been rarely used on its own for structure solution,[25] while more often it has been used to rescue subtle structural details at a later stage (because of the relative scattering power enhancement of selected elements, the simplicity of peak shapes and the lack of preferred orientation effects in transmission mode). Most of the potential workers in the field, however, deal mainly with conventional X-ray tubes and we will show that even in this 'unfortunate', but very common, situation, XRPD can afford valuable information at the moderate expense of the complexity of the affordable problems and of the accuracy of the results. Accordingly, and despite the fact that the most reliable results came from synchrotron[13,26] or joint synchrotron and neutron diffraction experiments,[16,27] the vast majority of *ab initio* structural studies so far reported has been performed with conventional equipment. There are many good reasons for such a fact. (*i*) Access to non-conventional sources might require long times and applications are conditioned to a high probability of success, which is obviously larger for a refinement than for an *ab initio* solution. As a result, more structural refinements than solutions have been performed by external users, while most of the synchrotron *ab initio* work is linked to beam scientists and their groups. Indeed, when applying for beam time one must convince the panel of reviewers that the proposal is sound (eventually leading to *publishable* results) and the more effective way to support an *ab initio* project is to demonstrate that it admits a solution, *i.e.* to solve it in advance from conventional data; this may be either a good reason for not applying or for not being allotted beam time.[28] (*ii*) When dealing with molecular compounds the weakness of intermolecular forces may result in specimen-limited patterns whose intrinsic peak widths cannot be reduced by high resolution sources. (*iii*) Conventional equipment grants a high probability of success if the proper methodology (tuned to the actual sample) is chosen and, being widespread and easily available, it allows structural chemists to tackle *immediately* the problems of their own interest.

The items raised above should not put into shadow unconventional sources since they become extremely valuable whenever beam tuneability (S), high intensity (S), time structure (S,N), parallel beam geometry (S) and different scattering cross sections (S,N) are required.

The *Ab Initio* Structural Problem

This section summarises our experience of moderately complex co-ordination compounds, for which only a plausible stoichiometry was known. It is not meant to be exhaustive, but should be taken as a representative example of the most commonly encountered problems.

It is well known that, from *poor* single-crystal data, it is still possible to obtain the gross molecular features, which can be useful for compound identification. On the contrary, the use of *roughly measured* powder diffraction patterns could easily lead to false, time-wasting solutions (if any at all), since the early steps of data processing (peak location, indexing and space group identification) require high accuracy; therefore, maximum effort should be put into sample preparation, equipment maintenance and alignment, *etc.* A detailed description of the general methodology used in our laboratory can be found in ref. 29, which reports the solution and refinement of a 24-atom structure [trimeric silver(I) 3,5-dimethylpyrazolate] from conventional XRPD data only. In the following, the steps required for *ab initio* structure analysis from PD data, which are pictorially represented in Scheme 1, are briefly discussed.

(*i*) Since the preliminary step is the accurate location of the diffraction peaks, the instrument should be tuned to the highest resolution available (smaller slits) and a specimen prepared as to minimise aberrations: a sieved sample, mixed with 10% by weight of an NBS Standard Reference Material, such as Silicon 640b[30] (as internal standard), should be deposited as a very thin layer (to avoid specimen transparency effects) on zero background plates[31] with the aid of a viscous, non-reacting medium (such as 5% collodion in amyl acetate solution, ensuring, in most cases, randomly oriented crystallites).

The Strategy for *ab initio* XRPD Structural Analysis

- Careful Sample Preparation: Thin Layer
- Narrow Optics Data Collection
- Peak Search (or Profile Fitting)
- Autoindexing + Cell Refinement
- Space Group Determination
- Careful Sample Preparation: Side Loading
- Wide Optics Data Collection
- Whole-pattern Profile Fitting
- Structure Solution
- Structural Model Completion
- Microstructural Model
- Final Rietveld Refinement

Scheme 1

(*ii*) The detection of peaks and the location of their maxima is often done by automatic peak search routines supplied by the equipment manufacturers. They usually work well, but it is often the direct (visual) inspection of the collected pattern that supplies extremely useful information about the presence of hidden peaks, shoulders or tails, which are of utmost importance for correct peak indexing. This crucial step is often overlooked (possibly because it is straightforward in single-crystal diffractometry), leading, perhaps, to fake unit cells and reflection indices, thus preventing any further characterisation of the sample. Sometimes, profile fitting[32] of a limited range of the pattern can afford better estimates of the peak location; it should be noted, however, that the latter technique is very rarely used as an *active* method for detecting small peaks underneath a complex cluster; in addition, convergence should be attained very slowly (with damping factors in the least-squares procedures as low as 0.10), because, in the absence of peak position constraints (which are only possible if the lattice metrics are known) high correlation between the refinable parameters, floating on an unconstrained R factor hypersurface, may occur.

(*iii*) The success of the autoindexing procedures,[33] for which a number of strategies and programs has been devised,[34] relies mostly on the accuracy of the measured d values, on their completeness and on the size of target unit cell. It is usually assumed that for the resolution and accuracy attainable with state-of-the-art X-ray powder diffractometers, only unit cells smaller than, say, 1500 Å^3 (if triclinic) can be confidently determined[35] (larger values being of course attained by higher symmetry lattices, or by the use of high resolution synchrotron sources). However, the presence of systematic absences, more than accidental ones, can impair the autoindexing process, since precious geometric information (from zero intensity lattice nodes) is thereby lost. The completeness of the observed peak list is often augmented by arbitrarily including low angle first-order reflections of strong observed peaks (assumed to be higher harmonics), which, for a variety of reasons, such as low sample illumination, asymmetric broadening by vertical divergence effects and/or low (or null) intensity, went unobserved.

(*iv*) In order to obtain accurate intensities, leading to the formulation of the correct structural model, a second data set is normally required. It is absolutely necessary to collect such data, with wider optics, on a truly randomised powder (by specimen spinning, side loading[36] or spray drying[37]) deposited as an 'infinitely thick' sample (thus avoiding scattering from the substrate and ensuring constancy of the scattering volume).

(*v*) The goal of extracting integrated peak areas from the powder pattern is normally attained by using whole-pattern profile fitting techniques,[38] some of which are optimised in order to overcome negative solutions for the measured intensities.[39] In addition to the refinable peak values, a number of highly correlating parameters is usually included in the least-squares matrix, leading often to ill-conditioned systems. We found it convenient to avoid fake minima by restraining all instrumental parameters to values obtained from single-peak analyses of well separated low angle reflections, and feel that relaxing such constraints should be done very carefully only when convergence is closely approached. This obviously holds also for lattice parameters, since the autoindexing procedure *and* the presence of a well aligned diffractometer normally guarantee very good estimates of the true values. If the powder diffraction data contain a few very strong peaks, dominating the whole pattern, the intensity extraction process might be heavily biased by their presence, and convergence might be very slow, sometimes requiring hundreds (!) of cycles in order to stabilise the solution. It is tentatively suggested that selectively discarding these portions of the pattern allows a better assessment of the intensities of the remaining peaks. Note, however, that the presence of such strong peaks might be indicative of residual texture effects and/or special spatial distribution of the heaviest scatterers, thus suggesting, among other things, the presence of a particular structural type (layers, rods, *etc.*).

(*vi*) The complexity of the diffraction pattern usually does not easily allow the detection of the systematic absences conditions, and only a limited number of null peaks can normally be assigned with certainty. This often implies that the space group assignment is difficult, particularly in the orthorhombic system (higher symmetries, in the realm of co-ordination compounds, are rare), where a bevy of systematic absences conditions can be present, and never definitive.

(*vii*) At this stage, *ab initio* structure determination from powder data involves a series of steps that mimics the sequence of events in a single-crystal (SC) study. However, since in a powder experiment the three-dimensional intensity data are projected into a single dimension, each individual step is neither easy nor certain and the whole process is still more empirical than exact. Structure solution can normally be achieved by using standard model building techniques, Patterson map interpretation, direct methods, or recently developed ad hoc methods such as real space scavengers, Monte Carlo methods, maximum entropy and likelihood, simulated annealing techniques and genetic algorithms.[40] The choice of the method which eventually leads to a partial structural model is based on the nature of the structural problem under study and tuned to it; however, within the realm of co-ordination compounds, we found that Patterson methods, not requiring a thorough statistical analysis for the phasing process as direct methods do, can afford significant information even when only low angle data are known with decent accuracy. Completion of the structural model, once approximate locations of the metal atoms have been determined, can normally be achieved by Fourier-difference methods, which, compared with the single-crystal ones, are rather noisy but can be improved by the sequential use of high-angle refinement of the metal atom coordinates and of the *true* scale factor, and structure factor calculations of the high *d* reflections on their basis. When possible, geometrical model building[41] and steric energy minimisation[42] in the crystal lattice can be used, leading to a limited number (possibly one) of approximate locations and orientations of the ancillary ligands and/or counter ions.

(*viii*) Strictly entangled with the structure solution process is the refinement of microstructural and structural parameters, which, upon success, will eventually lead to the final model. This last step, apart from a very few cases of high symmetry compounds which were refined by the so called two-stage method,[43] is normally associated with the Rietveld technique, and the sagacious use of chemically sound constraints,[44] and, given that extensive reports on this method appeared long ago,[7] will not be discussed any further.

A Glance at the Structural Use of Powder Diffraction Data

The amount of data easily collectable on any single crystal of good quality voids PD when samples of suitable size, crystallinity and stability are available. Nevertheless, there are cases where single crystals cannot be obtained due to the failure of all common methods of crystal growth, like slow evaporation, gel permeation, slow diffusion techniques or crystallisation from the melt. Given that *only the lack of suitable single crystals makes XRPD structural studies worthwhile*, we may attempt to circumscribe the meaningful use of XRPD as a structural tool to (*i*) insoluble, thermally unstable compounds which cannot be (re)crystallised from solution or from the melt; (*ii*) metastable phases destroyed or modified upon manipulation; (*iii*) twins, when the presence of double or multiple diffraction spots makes the 'single crystal' way of sampling the reciprocal lattice inefficient; (*iv*) very small crystals or crystal aggregates; (*v*) gas/solid, liquid/solid and solid-state reactions fragmenting and misorienting the coherent domains of the starting crystals but conserving the (poly)crystalline nature of the sample. The structural use of XRPD spans the whole Periodic Table but here we will discuss its growing importance in co-ordination chemistry which offers examples of all the above situations.

(*i*) Compounds which cannot be recrystallised

Many compounds, owing to their low solubility and/or poor thermal stability, cannot be (re)crystallised from solution or from the melt. Among them, polymers deserve particular attention because of their potential technological relevance. At the same time, they are ideal candidates for XRPD studies because their huge molecular size is often buried in the crystal lattice, *i.e.* their asymmetric unit normally consists of a single monomer and they 'appear' to XRPD as small systems. Indeed, XRPD has been successfully used in the structure determination of organic polymers,[45] and, more recently, for polymeric solid electrolytes[46] and metal-based polymers such as alkali metal cyclopentadienyls,[22b,47] $[Cu(CH_3S)]_n$,[48] $[MX_2(L^1)]_n$ (M = Mn–Cu; X = Cl or Br; L^1 = pyridazine)[49] and $[Ag(L^2)]_n$ L^2 = imidazolate).[50]

One-dimensional polymers containing transition-metal ions have been recently studied with the aim of discovering new materials with specific magnetic, optical, catalytic and structural properties.[51] New fundamental science can be expected to emerge as structure–property correlations are established for these systems. It is worth noting that organic and metal-based polymers differ in a substantial way, since their backbone chains possess different features: metal–ligand and metal–metal bonds are far less strong than backbone bonds of organic polymers and of main-group (inorganic) polymers such as polyphosphazenes, polysiloxanes and polysilanes. This normally implies that metal-based polymers are less stable as '(macro)molecules'; for instance, they can hardly be dissolved or melted without decomposition. Possibly, metal-based polymers grow only at the interface between the crystal and the solution and normally are much more crystalline than their 'organic' congeners. Moreover, folds, which are responsible for grain boundaries and amorphous regions of organic polymers, do not occur, since heavily folded metal-based chains are unstable with respect to chain breaking into small (cyclic) oligomers.

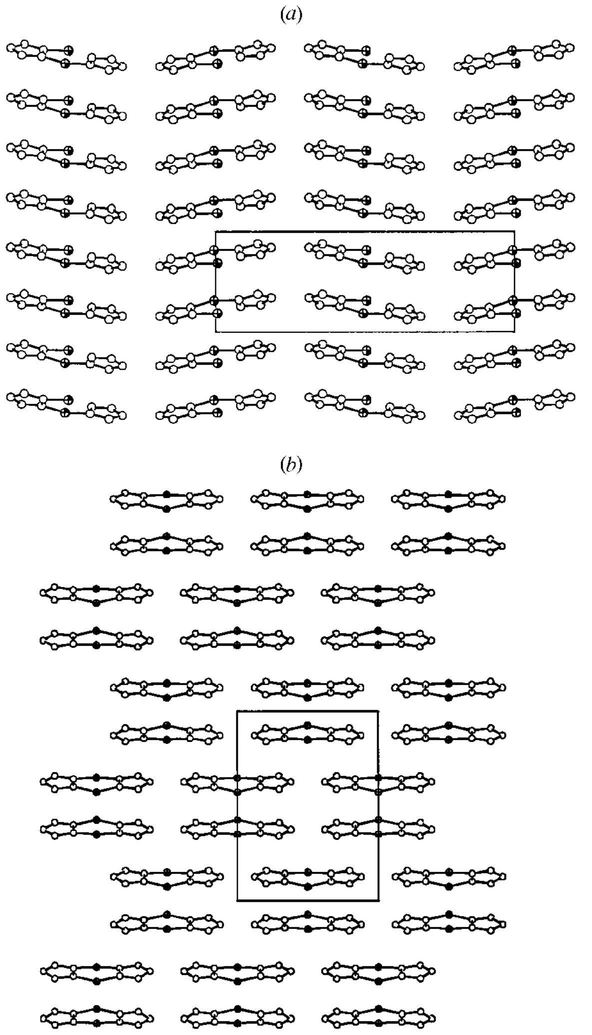


Fig. 1 Crystal packing (001 projection) of the α-$[Cu(pz)]_n$ (*a*) and β-$[Cu(pz)]_n$ (*b*) phases, showing the relative positions of the polymeric chains and their pseudo-rectangular (*a*) or pseudo-hexagonal (*b*) packing of chains of dimers, respectively

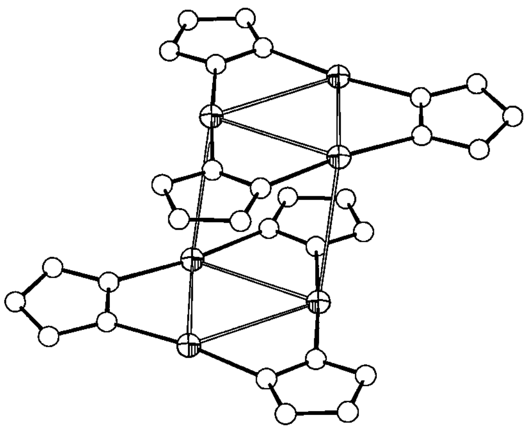
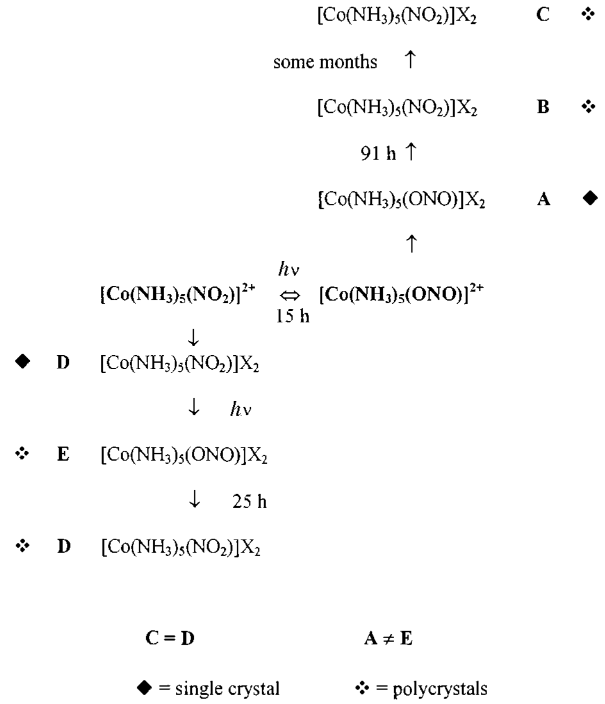


Fig. 2 An ORTEP[54a] drawing of the trimeric $[Ag(pz)]_3$ molecule. Two adjacent units are shown



Scheme 2

The $[Cu(pz)]_n$ and $[Ag(pz)]_n$ complexes (Hpz = pyrazole) have been known for a long time[52] but until recently their oligomeric or polymeric nature had never been clearly demonstrated. We were able to recognise four different phases,[53] namely: α-$[Cu(pz)]_n$ **1a**, $[Ag(pz)]_n$ **1b**, β-$[Cu(pz)]_n$ **2a** and $[Ag(pz)]_3$ **2b** whose structures are reported in Figs. 1 and 2. It is worth noting that **1a** and **1b** are isomorphous and that while we were working on this problem we believed for a long time that **2a** and **2b** were also a couple of isomorphous compounds, the XRPD pattern of **2b** presenting some features of that of **2a** when a few unindexed peaks are attributed to an impurity. Thus, we repeatedly attempted to refine the structural mode obtained for **2a** using the spectrum of **2b**. Being unable to obtain a reasonable R_{wp} value and after many failed attempts to obtain a 'pure' **2b** phase, we decided to reconsider the problem by allowing for a larger cell in the indexing procedure. We soon realised that there was a cell with a volume *ca.* $\frac{1}{2}$ larger than that of **2a**, accounting for all the observed peaks of the spectrum. Direct methods (SIRPOW)[54b] eventually lead to the correct formulation of **2b** as a trimeric compound which was readily modelled in GSAS[15a] as $[Ag(pz)]_3$ by imposing the proper constraints.

From this example it is clear that *XRPD alone allowed a strong chemical and structural belief* (the isomorphism of **2a** and **2b**) *to be discarded and led to the proposal of a totally different structural model* for **2b**, thus demonstrating that it is a convenient tool for proving or rejecting structural hypotheses. Similar results were obtained by XRPD on $[HgRu(CO)_4]_4$ (where the oligomer *vs.* polymer dichotomy was settled)[55] and on $[Ru(CO)_4]_n$[56] [where it was demonstrated that, at variance from what was previously inferred from the IR spectrum,[57] the repeating unit was a *trans*-D_{4h} rather than a *cis*-C_{2v} $Ru(CO)_4$ fragment]. Moreover, in the latter case, the interpretation of the anisotropic peak broadening (full width at half maximum, at low angles, in the 0.40–2.0° range) allowed the estimation of the intermolecular strain and of the average chain length of *ca.* 90 monomers.

(*ii*) Metastable phases

Polymorphism is the ability of a compound to crystallise in more than one distinct crystal phase.[58] At a given temperature, only one such distinct phase is thermodynamically stable, the other being at most metastable. Metastable phases sometimes have relatively short lifetimes; moreover, even when they are long lived (for kinetic reasons, owing to the large activation energies often associated with solid-state transformations) they are difficult to (re)crystallise since manipulation often pushes the phase transformation toward the most thermodynamically stable polymorph.

We have studied the solid-state linkage isomerisation[59] $[Co(NH_3)_5(NO_2)]X_2 \rightleftharpoons [Co(NH_3)_5(ONO)]X_2$ (X = Cl or Br), following the reverse ONO–NO_2 isomerisation (see Scheme 2), which has first-order kinetics with a half-life of *ca.* 25 h at room temperature. X-Ray powder diffraction is the only tool for obtaining structural information about **E** since irradiation of single crystals of **D** affords only a powdered sample of **E**. Noteworthy, we have discovered that **A**, which is crystallised from irradiated solutions of $[Co(NH_3)_5(NO_2)]Br_2$, has a different crystal and *molecular* structure from **E**. As a matter of fact, **A** and **E** are conformational polymorphs;[60] they do not share similar lattices and differ in the nature of the Co–O–N linkage (linear in **E**, bent in **A**).

What is relevant here is to ascertain the degree of reliability of XRPD in supporting such unusual structural features (all the other known nitrito derivatives have bent Co–O–N linkages), given that the disorder of the terminal oxygen atom of the nitrito group could cast some doubt on the correctness of the chosen space group (*Cmcm*). We must point out that a linear Co–O–N linkage might appear unusual, but there is nothing unreasonable in it since the Co–O–N bending energy is expected to be quite small, hence easily overcome by the steric requirements imposed by the reaction cavity of the lattice of **D**.

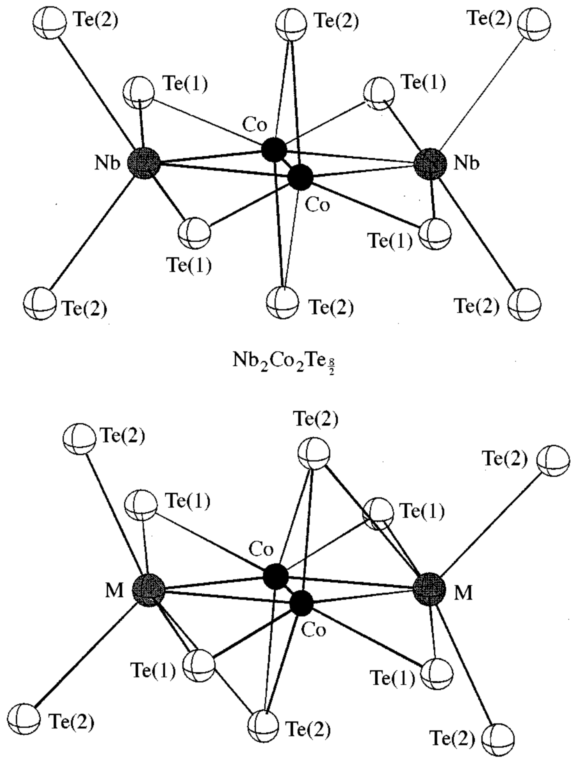
The major evidence for a linear Co–O–N linkage comes from Fourier-difference maps[59] which, when the nitrito phase was refined in the *Cmcm* space group omitting the atoms of the ONO fragment, showed the location of two peaks, of approximate height of 4 and 3 e Å^{-3} (assigned to O and N atoms), on the two-fold axis, while no localised electron density higher than 0.35 e Å^{-3} could ever be detected for the second oxygen atom, which was then assumed to be disordered over four (*mm*2 symmetry related) positions about the *b* axis. This is consistent with the analysis of interatomic contacts in the crystal lattice and with a semiquantitative potential energy computation performed with SMILE[41] which clearly showed a four-fold barrier upon rotation of the O–N–O moiety about the Co–O axis (which, interestingly, rises in energy with the bending of the Co–O–N linkage). Moreover, all the attempts to obtain a more common set of geometric parameters, either by removing selected symmetry elements about the ONO group (and lowering the space group symmetry to $Cmc2_1$, $C2/c$ and Cc) and/or by forcing a bent Co–O–N co-ordination and/or a shorter Co–O distance, lead to heavily worsened agreement factors and to Fourier-difference maps invariably showing the two strong peaks on the *b* axis. Hence, the reliability of the proposed model lies in the coherent picture offered by packing analysis, potential energy computations, Fourier-difference maps and by the failure to obtain better agreement on refining different models.

A structural XRPD study on a metastable co-ordination compound has been also reported by Louër and co-workers.[61] Another representative example, triclinic $[Pd(pz)_2(Hpz)_2]_2$, which can be selectively synthesised as powders but, upon recrystallisation, affords uniquely its monoclinic polymorph, is discussed in section (*v*) from a different perspective.

(*iii*) Twins

Twins are regular aggregates consisting of individual crystals of the same species joined together in some defined mutual orientations. A recent classification cuts the twin kingdom in two. Twin–lattice symmetry (TLS) twins show a single orientation of the reciprocal lattice so that they give rise to single diffraction spots. Twin–lattice quasi-symmetry (TLQS) twins are characterised by two or more reciprocal lattices differently oriented giving rise to double or multiple diffraction spots.

The presence of twinning makes structure determination difficult and unreliable even from ‘single’ crystal data of (apparent) good quality. In this case, powder diffraction is well suited because the individual twins are treated as *independent* crystallites with their diffraction peaks lying at identical θ values. As a consequence, *the presence of twinning does not affect the powder patterns* (meaning, in turn, that it is impossible to detect twins by XRPD); if the size of the problem is not too large, crystal structures can be successfully solved and refined with XRPD, this being particularly significant for TLQS twins. A twinning problem was faced by XRPD in the structure analysis of the copper analogues of the *ordered* $[NiX_2(4,4'\text{-bipy})]$ (X = Cl or Br, 4,4′-bipy = 4,4′-bipyridine) phases[62] and, with larger emphasis, of $MCoTe_2$ (M = Nb or Ta).



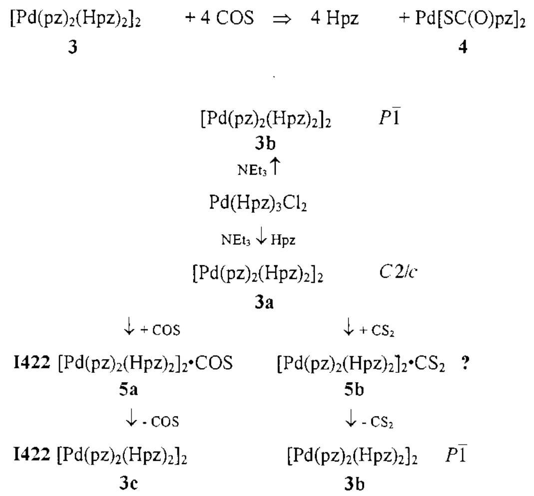
$Nb_2Co_2Te_{\frac{8}{2}}$

$M_2Co_2Te_{\frac{8}{2}}$ M = Ta or Nb

Fig. 3 Perspective view of the layered $TaCoTe_2$ compound

The crystals of $TaCoTe_2$ appear as very thin platelets,[63] in agreement with the layered structures of a number of ternary tellurides reported in the literature. Independent of the actual thickness of the chosen samples, all (apparently single) crystals mounted on a four-circle diffractometer gave intense Bragg reflections and an orthorhombic unit cell similar to that of the reported Nb analogue, but with very poor estimated standard deviations. A closer look at the most intense peaks revealed, however, that they were narrow in θ, but several degrees wide in ω, and (for some classes) possessed a double-maxima nature. On selecting a coherent set of maxima, a monoclinic unit cell was determined and this led to the conclusion that all crystals of $TaCoTe_2$ were twinned samples of a truly *monoclinic* phase. Accordingly, we decided to use XRPD to study $TaCoTe_2$. The XRPD pattern immediately confirmed the monoclinic unit cell and a P-RISCON[64] run led to the structure solution which is reported in Fig. 3.

The monoclinic distortion, with respect to an idealised orthorhombic phase, consists of the asymmetrisation of the Ta–Te(2) distances and a shear of the Te(1) row with respect to the Te(2) one. It should be emphasised that the aforementioned bending represents the *chemical* clue for the existence of the monoclinic phases. In fact, starting from the orthorhombic phase, the bending of the Te(2) atom toward one Nb atom determines a phase transition of displacive type, which lowers the crystal symmetry to monoclinic. The equally probable bending toward the second Nb atom of each cluster would create an identical, but differently oriented, layer. Therefore, the stacking of adjacent layers having opposite bending directions causes the observed twinning. Note that equal probability of this bending does not imply a random sequence of the two types of layers (A,B), which would produce a disordered structure (*e.g.* . . . ABAABABBAB . . .) *i.e. microtwins*; rather, the different



$[Pd(pz)_2(Hpz)_2]_2$ + 4 COS ⇒ 4 Hpz + $Pd[SC(O)pz]_2$
3 **4**

$[Pd(pz)_2(Hpz)_2]_2$ $P\bar{1}$ **3b**
$\xleftarrow{NEt_3}$ $Pd(Hpz)_3Cl_2$ $\xrightarrow{NEt_3,\ Hpz}$
$[Pd(pz)_2(Hpz)_2]_2$ $C2/c$ **3a**
↓ + COS ↓ + CS_2
I422 $[Pd(pz)_2(Hpz)_2]_2{\cdot}COS$ **5a** $[Pd(pz)_2(Hpz)_2]_2{\cdot}CS_2$? **5b**
↓ - COS ↓ - CS_2
I422 $[Pd(pz)_2(Hpz)_2]_2$ **3c** $[Pd(pz)_2(Hpz)_2]_2$ $P\bar{1}$ **3b**

Scheme 3

energetics at the interfaces between layers (AA or AB) cause the formation of conglomerated crystallites, containing large ordered domains (... AAAAABBBBB ...), *i.e. macrotwins.*

As a further example, even if the complete structural model of (η^5-C_5Me_5)ReO_3 was eventually refined from (several) 'single crystal' data, its microtwinned nature has been discovered by the investigation of the *whole* reciprocal space intrinsic to the PD technique;[65] indeed, the violations of systematic absences conditions (in the PD pattern!!) and the presence of asymmetrically broadened reflections suggested the correct paracrystallinity model, *a rare case of a two-dimensional polytypism,* which has been later supported by XRPD simulations (DIFFAX,[66] DISCUS[67]). Eventually, (para)crystals of (η^5-C_5Me_5)ReO_3 resulted, containing *ordered* chains (of discrete molecules stacked, head-to-tail, along one crystal axis) statistically packed (in the other two dimensions) by two different symmetry (packing) operators.

(*iv*) Very small crystals or crystal aggregates

Sometimes, chemical species, soluble in a number of solvents, can be crystallised only as very small (maximum dimensions <20 μm) crystals, or give dendritic aggregates from which monocrystals cannot be easily isolated. It has been recently shown that in such cases the use of synchrotron radiation and even of laboratory instruments, if equipped with rotating anodes, X-ray enhancing optics (multigraded mirrors and/or focusing collimators) and CCD area detectors, allows the collection of single-crystal data (which are however affected by troublesome counting statistics).[68] However, beyond the limited access to any of the above mentioned facilities, the problem of handling and manipulating the specimen, as a limiting step, still remains. Thus, if the complexity of the system under study is not too high and the sample can be prepared as a single phase in sizeable quantities (see above), XRPD, which can be applied to crystallites of less than 1 μm, can offer a viable alternative. For appropriate examples dealing with this problem see the study of Louër and co-workers[69] and ref. 70.

(*v*) Gas/solid, liquid/solid and solid-state reactions

Differently from reactions in solution, solid-state reactions occur within a definite constraining environment, the crystal lattice, which can control both the kinetic features of the reaction and the nature of the products. The reaction product is not necessarily the thermodynamically most stable product available to the system, but it is rather the one dictated by the reaction pathway available in the constraining environment of the solid.[71] Noteworthy, this behaviour extends also to gas/solid and liquid/solid reactions whenever the diffusion of the reactant (gas or liquid) does not disrupt (or dissolve) the crystal lattice. In particular, reactions between small gaseous molecules and solid transition-metal complexes may lead to the formation of species not observable in solution (metastable reaction intermediates) and, consequently, to important mechanistic breakthroughs. Indeed, if the diffusion takes place throughout the crystal, gas/solid reactions could occur with partial retention of crystallinity and may afford *addition* products more easily than their solution analogues, since the crystal lattice should prevent the dissociation of large fragments.

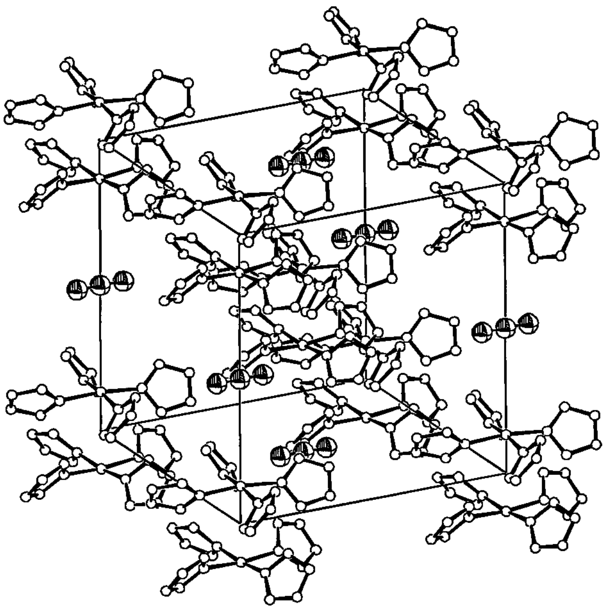


Fig. 4 An ORTEP drawing of the unit cell content of $[Pd(pz)_2(Hpz)_2]_2{\cdot}COS$, showing *clathrated, unco-ordinated* COS molecules (dumbbells at 0, 0, $\frac{1}{2}$). For the sake of clarity, methyl and hydrogen atoms are omitted and only a single orientation of the COS molecules, disordered about a four-fold axis, is drawn

The complex $[Pd(pz)_2(Hpz)_2]_2$ **3** (from here on, Hpz = 3,5-dimethylpyrazole), when dissolved in CH_2Cl_2, reacts with COS affording the *insertion* product $Pd[S(CO)pz]_2$ **4** which has been characterised by single-crystal X-ray diffraction and has a ν_{CO} of 1658 cm^{-1}.[72] In contrast, when the same reaction is attempted in the solid state, by mixing (crystalline) powdered **3a** with liquid COS (at 193 K), the resulting (*still crystalline*) product has a ν_{CO} of 2048 cm^{-1} and analyses as $[Pd(pz)_2(Hpz)_2]_2{\cdot}COS$ **5a** (see Scheme 3).

Compound **3** has been structurally characterised in three polymorphic phases using SC X-ray diffraction (**3a**) and XRPD (**3b** and **3c**). It is worth noting that **3b** has a 'huge' asymmetric unit (*ca.* 1300 Å^3) and that its successful *ab initio* XRPD structure characterisation has been performed through Patterson deconvolution and extensive molecular modelling (possible because of the detailed knowledge of the molecular shape of **3** obtained from the SC study of **3a**). However, our principal aim was the XRPD structural characterisation of **5a**, which we thought contained the elusive end-on co-ordination mode (–SCO) stabilised by the crystal lattice, since it has been claimed that a small decrease (2048 *vs.* 2051 cm^{-1}) of the ν_{CO} value (with respect to that of free COS) is indicative of end-on co-ordination.[73] Again, deconvolution of the Patterson map allowed the location of the unique independent Pd atom in the asymmetric unit while molecular modelling allowed the build up of the starting model which was then refined imposing suitable restraints. At this point a Fourier-difference map showed unequivocally that the COS ligand was *not co-ordinated* to the $[Pd(pz)_2(Hpz)_2]_2$ unit but rather it was *clathrated* into the host lattice of the $[Pd(pz)_2(Hpz)_2]_2$ molecules (Fig. 4). Interestingly, the diffusion of COS into the lattice of **3a** promotes a phase transformation and the inclusion compound **5a** has a tetragonal lattice. Moreover, at room temperature, **5a** slowly loses

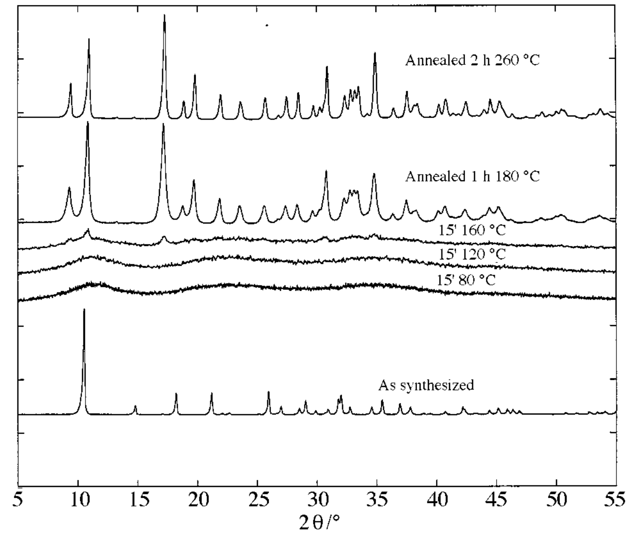


Fig. 5 The XRPD patterns (bottom to top) of the pristine [Ag(pymo)]$_n$·2nH$_2$O polymer and of its solid-state dehydration products under progressive heating; top curves: the crystalline hexamer [Ag(pymo)]$_6$

COS and transforms into the third polymorph **3c**, the structure of which has also been determined by XRPD.

We have also studied[74] the solid-state dehydration of the [Ag(pymo)]$_n$·2nH$_2$O polymer (Hpymo = 2-hydroxypyrimidine).[75] Differential scanning calorimetry and thermogravimetric analysis showed that (*i*) it readily loses water in the 80–110 °C range ($\Delta H = 101$ kJ mol^{-1}), (*ii*) a weak esotherm, not accompanied by weight losses, is present at about 150°C ($\Delta H = -4.9$ kJ mol^{-1}) and (*iii*) complete thermal decomposition (to metallic silver) occurs at about 300 °C. X-Ray powder diffraction showed that progressive heating generates an amorphous phase which transforms, above 150 °C, into a white (poly)crystalline phase (see Fig. 5). Infrared monitoring (Nujol mulls) confirmed the loss of water and the formation of a slightly different absorption pattern, which we originally attributed to the anhydrous [Ag(pymo)]$_n$ polymer. However, rather surprisingly, our XRPD analysis led to the discovery of a novel cyclic, hexameric, chair-like compound [Ag(pymo)]$_6$, of crystallographic C_{2h} symmetry.

In summary, XRPD is a fundamental tool for characterising solid-state reactions which often result in unexpected products: (*i*) in the first example, shedding new light on previous claims of end-on co-ordination of CO$_2$, COS and CS$_2$ from small decreases of the ν_{CO} frequencies; (*ii*) in the second example, allowing us to demonstrate that the foreseen anhydrous [Ag(pymo)]$_n$ polymer was indeed a cyclic oligomer. In principle, prolonged efforts and non-standard crystallisation techniques could afford crystals of suitable quality, thus putting into the shade the above mentioned results. However, when a crystalline phase results only from a solid-state transformation, such as β-[CuCl$_2$(4,4′-bipy)]$_n$[62] or the above [Pd(pz)$_2$(Hpz)$_2$]$_2$·COS, it is likely that single crystals will never be grown and that powder diffraction will remain the ultimate tool for structural characterisation.

Conclusion

Unconventional sources are rare and expensive; therefore, laboratory instruments are a profitable choice to scrutinise many related phases, to optimise sample preparation (which is not straightforward) and to select the most promising conditions for further NPD or SRPD experiments, *if they are really worthy*. As a matter of fact, the poor shape of the instrumental profile and the low intensity of X-ray tubes do not necessarily hamper reasonable data from being obtained and reasonable structural models to be refined from XRPD data. Moreover, there are many significant phases whose intrinsic diffraction profiles are too broad to take any advantage from the use of high resolution techniques.

From the analysis of the literature and of the above examples, it appears that: (*a*) the upper limit of non-hydrogen atoms in the asymmetric unit which can be successfully detected with *good* conventional equipment can be estimated to be about 40 (asymmetric unit volume of about 800 Å^3); this rather optimistic estimate is probably more valid for crystal phases containing molecules with a few heavy atoms, known stereochemistries and rather rigid, easy to model, ligands; (*b*) synchrotron radiation data (particularly when combined to neutron diffraction measurements) may allow problems twice as complex to be tackled; and (*c*) there is a gap between the complexity of the structures which can be solved and those which can be eventually refined by the Rietveld method (again, a factor of *ca.* 2).

Summarising, we think that, despite the fact that many geometric details are lost along with the heavy ‘idealisation’ of the structural model, XRPD still affords plenty of useful information such as paracrystallinity, molecular shape, heavy atom stereochemistry, rough interatomic distances (and angles) and crystal packing. Of even greater importance, XRPD is no longer bound to validate (or reject) prefigured hypotheses but, being a valuable, sometimes *irreplaceable*, *active* structural tool, can be profitably used to *discover* new structual features.

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