Powder Route to Crystal Structures: X-Ray Powder Diffraction Determination of Polymeric Silver Imidazolate†

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Silver imidazolate has been synthesized and its solid-state structure determined, ab initio, from conventional X-ray powder diffraction data only. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 5.5759(4)$, $b = 6.7452(4)$, $c = 22.174(1)$ Å, $U = 834.0(1)$ Å^3, $Z = 8$, $D_c = 2.786$ g cm^{-3}. The structure was solved by a real-space scavenger technique and refined by the Rietveld method down to R_p and R_f values of 0.062 and 0.027, respectively, for 4401 data points (1262 reflections) measured at room temperature in the 17–105° (2θ) range. The crystal structure of [{Ag(im)}$_n$] (Him = imidazole) consists of a complex packing of polymeric chains folding about the crystallographic c axis, containing linearly co-ordinated silver atoms joined by imidazolate fragments. Short interchain Ag···Ag contacts [3.161(4) Å] were observed.

Neutral heterocyclic diazines, such as pyrazine, pyrimidine and pyridazine, are known to bond to different metal centres, acting as 'exobidentate', rather than 'endobidentate' ligands;[1] analogously, deprotonation of pyrazoles and imidazoles yields azolates with excellent bridging capabilities.[2] The absence of chelation allows, therefore, the formation of oligomeric and/or polymeric frameworks displaying a wide variety of geometries, such as those found in trimeric, tetrameric, hexameric and polymeric Group 11 pyrazolates.[3] In addition, the recent characterization of some one-dimensional polymers[3] or two- or three-dimensional nets[4] possessing the same stoichiometry has shown that easily accessible polymorphs can be selectively synthesized.

Many of these species are of interest for their potential role in multi-metal-centred catalysis, as precursors of catalytically active species or as catalysts on their own.[5] In addition, one-dimensional polymers are particularly attractive in connection with material science; the intrinsic anisotropy of the intra- vs. inter-chain interactions, bridging the gap between molecular features and bulk properties, may give rise to electrical, optical and magnetic properties which are a complex function of their chemical, electronic and architectural features.[6]

In spite of the relevance of a detailed structural characterization for the interpretation of physical properties, for many species, the polymeric nature of which has been inferred by their insolubility and thermal stability, only hypothetical structures were proposed on the basis of spectroscopic assignments and/or low-temperature magnetic susceptibility measurements. It is worth noting that, at variance from low-nuclearity species, which can normally be studied by conventional single-crystal methods, most polymeric complexes can only be obtained as microcrystalline materials; therefore, all structural information must be extracted from powdered samples only.

The appearance and availability of synchrotron radiation

and time-of-flight neutron sources have favoured, in the last decade, the rapid development of experimental and numerical techniques for ab-initio structure determination (not merely Rietveld refinement) from powder diffraction data.[7] This methodology, initially applied to 'classical' inorganic compounds only, has been recently proved successful in unravelling the structures of a few organic[8a] and organometallic[8b] compounds, even when coupled with standard laboratory equipment data.[3,8,9]

Although a high accuracy level cannot easily be obtained, it has often been noted[3,9] that, using powder diffraction data only, the average bond distances, overall topology, molecular conformations and crystal packing can be well determined. This is particularly true if the presence of 'rigid' ligands lowers the structural complexity to be modelled, by introduction of chemically sound geometrical constraints. Accordingly, and following our recent X-ray powder diffraction studies on the polymeric forms of Ru(CO)$_4$,[10] [MX$_2$(pydz)] (M = Mn, Fe, Co, Ni or Cu; X = Cl or Br; pydz = pyridazine)[9] and Cu and Ag pyrazolates,[3] we now report on the synthesis of a polymeric silver imidazolate phase and on its crystal structure determination from powder diffraction data.

Experimental

General Comments.—Imidazole and silver nitrate (Aldrich) were used as supplied. Elemental analyses was carried out at the Microanalytical Laboratory of this University. Infrared spectra (Nujol mulls) were recorded on a Bio-Rad FTS 7PC instrument. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC 7 instrument. Electron impact (EI) mass spectra were collected on a VG 7070 EQ instrument.

Synthesis of [{Ag(im)}$_n$].—To a solution of imidazole (Him) (2.00 g, 29.4 mmol) and AgNO$_3$ (2.50 g, 14.7 mmol) in water (40 cm^3) maintained at room temperature 3 cm^3 of an aqueous solution of NH$_3$ (25%) were added; a white precipitate immediately formed. After 30 min stirring, it was filtered off, washed with water (40 cm^3), methanol (20 cm^3) and dried under vacuum (3.41 g; yield > 97%) (Found: C, 20.45; H, 1.70; N,

16.20. Calc. for $C_3H_3AgN_2$: C, 20.60; H, 1.75; N, 16.00%). IR: 3109w, 1171m, 1092s, 856m, 826m, 774m, 756s, 747s and 663s cm^{-1}. The synthesis of the copper(I) analogue was also attempted, but only badly diffracting (and easily oxidizable) powders of [{Cu(im)}$_n$] were obtained. Work is in progress to characterize better this species.

X-Ray Structure Analysis.—X-Ray powder diffraction (XRPD) data were measured with Cu-Kα radiation (λ = 1.5418 Å) on a Rigaku D-III MAX horizontal-scan diffractometer equipped with parallel Soller slits, a graphite monochromator in the diffracted beam, a Na(Tl)I scintillation counter and pulse-height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Slits used: (divergence) 1.0°, (antiscatter) 1.0°, (receiving) 0.3°.

The white [{Ag(im)}$_n$] powders were gently ground in an agate mortar, then cautiously deposited in the hollow of an aluminium sample holder using the side-loading technique,[11] in order to minimize preferred orientation effects in the plane normal to the scattering vector. Data were collected, at room temperature, in the 5–105° (2θ) range, step scan width $\Delta 2\theta$ 0.02°, the entire run lasting about 15 h.

Standard peak-search methods were used for location of the diffraction maxima. Data were indexed on the basis of 21 observable lines using the trial-and-error algorithm implemented in TREOR;[12] an orthorhombic system with approximate cell dimensions 5.58 × 6.76 × 22.19 Å was detected [$M(21)$ = 19;[13] $F(21)$ = 33 (0.013, 49)[14]]; density calculations led to Z = 8. The structure was solved as follows: first, a full-profile pattern decomposition was performed using ALLHKL;[15] owing to the high degree of overlap of several close-lying reflections, the space group assignment, based on the systematic absences, was ambiguous; therefore, several possibilities had to be tested. The correct solution was eventually found when the first 75 peaks (corresponding to 46 observations) were fed to P-RISCON[16] (and the $P2_12_12_1$ space group chosen), which succeeded in locating two independent silver atoms [$R(F^2)$ = 0.20]; at this stage, full-profile Rietveld refinement afforded R_p = 0.177. The remaining atoms were found by successive Fourier-difference maps / Rietveld least-squares refinements (using GSAS[17]) and geometrical considerations.

Atomic scattering factors have been taken from the internal GSAS library.[17] The background level has been modelled by a six-term cosine Fourier series; the profile shape has been described by a pseudo-Voigt[18] function and an asymmetry

parameter for the low-angle reflections accounting for the finite slit size. The angular dependence of the full widths at half maximum of the observed peaks was modelled following Caglioti *et al.*[19] for the Gaussian component (with V set to zero), and by a refinable Lorentzian (tan θ dependent) broadening term.[20] The preferred orientation correction, in the formulation of March[21] and Dollase,[21] was best effective if the 00l direction was selected. In addition, an overall isotropic thermal parameter model was chosen, the contribution of the hydrogen atoms to the scattering factors neglected and chemical constraints on the imidazole rings (C–C = C–N = 1.38 Å, internal angles = 108°) added, resulting in R_p, R_{wp} and R_F values of 0.062, 0.083 and 0.027, respectively. In the final stages of the refinement (57 refined parameters), only the data in the 17–105° (2θ) range, corresponding to 1262 reflections, were used, for which instrumental aberrations are minimized. The maximum peak in the final Fourier-difference map was 0.48 e Å^{-3}. A plot of the observed and calculated spectra is shown in Fig. 1. Crystal data and details on the refinements are collected in Table 1, fractional atomic coordinates in Table 2 and relevant bond lengths and angles are supplied in the caption of Fig. 2.

Results and Discussion

The preparation of [{Ag(im)}$_n$] was originally reported by Bauman and Wang,[22] who used diluted NaOH instead of aqueous ammonia. Their synthesis, therefore, closely resembles the preparation of Buchner's silver salt, [{Ag(pz)}$_n$] (Hpz = pyrazole).[23] The polymeric nature of silver(I) and copper(I)[24] imidazolates was originally suggested on the basis of geometrical considerations and physico-chemical properties.

Differential scanning calorimetry shows that [{Ag(im)}$_n$] is stable up to about 260 °C, where decomposition begins; no crystal-to-crystal transformation, such as the $\beta \rightarrow \alpha$ phase transformation of the [{Cu(pz)}$_n$] polymers,[3] is observed in the measured range. The absence of significant peaks in the EI mass spectrum of [{Ag(im)}$_n$] is in agreement with the unlikely formation of 'volatile' oligomers. Indeed, whilst many Cu^I and Ag^I pyrazolates exist in the mass spectrometer mainly as trimers (dimers and monomers being also evident in their fragmentation patterns), the larger imidazolato bite angle (*ca.* 144 *vs.* 72°) only allows the existence of 'heavyweight' metallacycles with six (or more) [Ag(im)] monomers.

Polymeric [{Ag(im)}$_n$] readily reacts with neutral ligands, such as PPh$_3$, affording polymeric adducts of general formula [{Ag$_2$(im)$_2$(PPh$_3$)$_m$}$_n$] (m = 2 or 3). Their complete chemical, spectroscopic and structural characterization are in progress.

The structural determination of [{Ag(im)}$_n$] from powder diffraction data only yielded the structural motifs depicted in Fig. 2, *i.e.* a complex packing of polymeric chains containing linearly co-ordinated silver atoms bridged by imidazolate ligands. A few other binary metal imidazolates are known,

Table 1 Crystal data and refinement details for [{Ag(im)}$_n$]

Formula	$C_3H_3AgN_2$
M	174.94
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	5.5759(4)
b/Å	6.7452(4)
c/Å	22.174(1)
U/Å^3	834.0(1)
Z	8
D_c/g cm^{-3}	2.786
$F(000)$	656
μ(Cu-Kα)/cm^{-1}	380.41
N_{data}	4401
N_{refl}	1262
N_{var}	57
R_p	0.062
R_{wp}	0.083
R_F	0.027

$R_p = \Sigma|y_{i,o} - y_{i,c}|/\Sigma y_{i,o}$, $R_{wp}^2 = \Sigma w_i(y_{i,o} - y_{i,c})^2/\Sigma w_i y_{i,o}^2$ and $R_F = \Sigma|F_o - F_c|/\Sigma F_o$, where $y_{i,o}$ and $y_{i,c}$ are the observed and calculated point intensities, respectively, and w_i is a statistical weighting factor, taken as $1/y_{i,o}$.

Table 2 Fractional atomic coordinates for [{Ag(im)}$_n$] with estimated standard deviations in parentheses

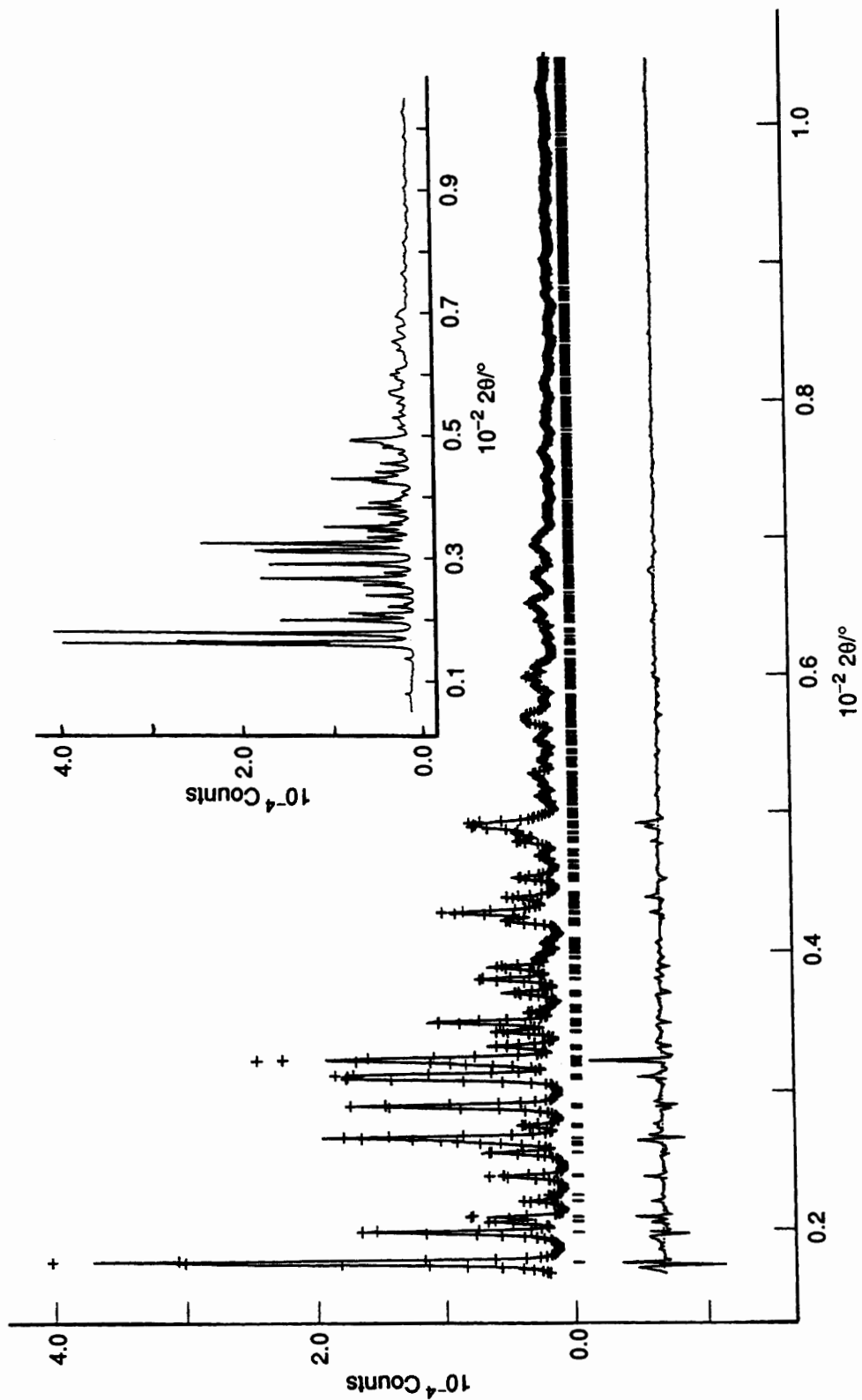| Atom	X/a	Y/b	Z/c
Ag(1)	−0.147 7(4)	0.929 5(4)	0.378 20(18)
Ag(2)	0.092 5(4)	0.895 3(4)	0.115 25(16)
N(1)	−0.194(5)	0.847(3)	0.288 5(5)
N(2)	−0.123(4)	0.859(4)	0.189 4(8)
N(3)	0.138(3)	1.039(3)	0.553 2(11)
N(4)	−0.082(5)	0.972(4)	0.471 5(6)
C(1)	−0.035(3)	0.913(4)	0.245 2(13)
C(2)	−0.390(3)	0.767(3)	0.259 1(11)
C(3)	−0.337(4)	0.761(3)	0.198 3(9)
C(4)	0.129(4)	1.057(5)	0.491 2(11)
C(5)	−0.075(5)	0.955(4)	0.572 1(6)
C(6)	−0.207(3)	0.907(4)	0.521 5(13)

Fig. 1 Observed (+) and calculated (solid line) XRPD pattern for [{Ag(im)}ₙ]. Reflection markers and difference plot are at the bottom. Experimental data are shown in the insert

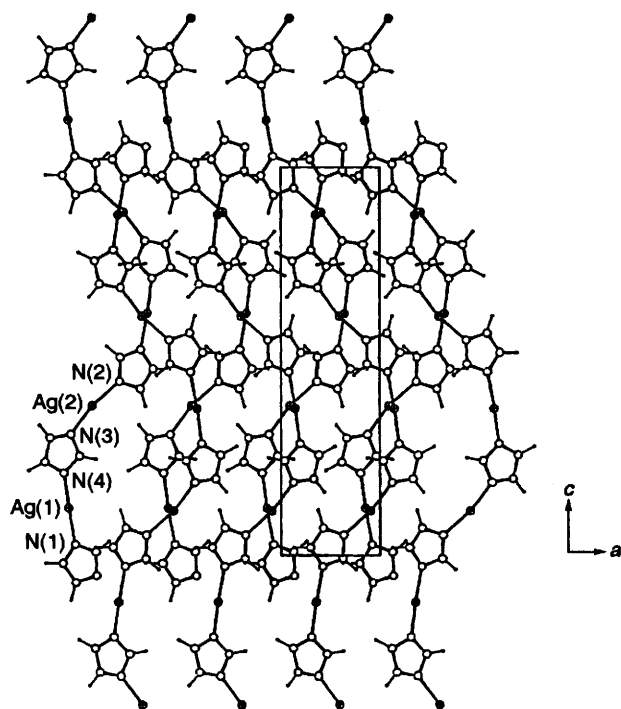**Fig. 2** Crystal packing of the [{Ag(im)}$_n$] chains, viewed down the b axis; the unit cell dimensions are marked. Relevant bond distances (Å) and angles (°): Ag(1)–N(1) 2.08(1) Ag(2)–N(2) 2.05(1) Ag(2)–N(3) 2.08(1), Ag(1)–N(4) 2.12(1), Ag(1) $\cdots$ Ag(2) 3.161(4), N(1)–Ag(1)–N(4) 171.8(8), N(2)–Ag(2)–N(3) 167.6(1)

Fig. 3 Crystal packing of the [{Ag(im)}$_n$] chains, viewed down the c axis, showing the herringbone packing of the chains in the ab plane

namely [Cu(im)$_2$],[25] [Co(im)$_2$],[26] [Zn(im)$_2$][27] and [Fe(mim)$_2$][28] (Hmim = 2-methylimidazole), possessing very complex three-dimensional nets. The 1:1 stoichiometry of [Ag(im)], however, guarantees that only cyclic, oligomeric species or one-dimensional chains can be formed. The polymeric chains of [{Ag(im)}$_n$] (containing two crystallographically and stereochemically inequivalent imidazolate rings) lie about the screw axis aligned with c (which represents, therefore, a four monomer unit). The [{Ag(im)}$_n$] chains are essentially flat [the dihedral angles between adjacent imidazolato rings being ±8(1)°] and lie approximately in the (1,2,0) and (1,−2,0) planes, packing therefore (in the ab plane, see Fig. 3) in the herringbone mode (with the spine direction along a), which is a common packing motif for many organic polymers possessing liquid-crystalline behaviour.[29] The overall conformation of each chain can be described, using the nomenclature developed in ref. 3 for oligomeric and polymeric pyrazolates, by a cis-trans-cis-trans sequence. In contrast, the hydrogen-bonded structure of imidazole (where H$^+$ formally replaces the Ag$^+$ ions), as determined from single crystals and neutron diffraction data,[30] folds about its c axis, with a dihedral angle of 60.2°, in the all-trans mode. The recent reports of the [{Ag(pz)}$_n$][3] and [{[Ag(hpym)]·2H$_2$O}$_n$][31] (Hhpym = 2-hydroxypyrimidine) polymers (the latter containing 1,3-diazaheterocycles formally equivalent to imidazolates) also show chain conformations in the all-trans mode.

Short d^{10}–d^{10} contacts are often encountered in the solid-state chemistry of coinage metals,*,[32] which can afford supramolecular structures. While slabs or dimers of chains could be seen in the crystal packing of α-[{Cu(pz)}$_n$]–[{Ag(pz)}$_n$] and β-[{Cu(pz)}$_n$],[3] respectively, the topology of the intermetallic interactions gives [{Ag(im)}$_n$] a three-dimensional character, since each chain suffers from short

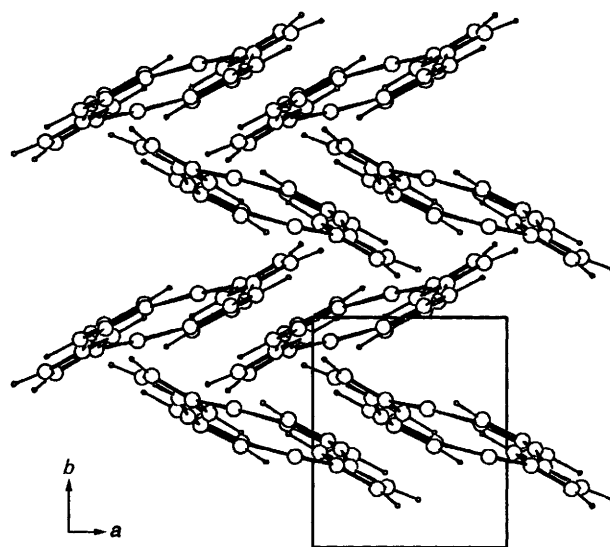metal–metal interactions [Ag $\cdots$ Ag 3.161(4) Å] with four different neighbouring chains. Within this class of compounds, somewhat longer Ag $\cdots$ Ag interchain interactions have been observed, i.e. 3.27 and 3.30 Å, for [{Ag(pz)}$_n$][3] and [{[Ag(hpym)]·2H$_2$O}$_n$],[31] respectively.

We feel that the recently established practice of coupling XRPD and molecular mechanics in the realm of organic polymers[33] can be extended straightforwardly to the characterization of inorganic polymers. In fact, since XRPD affords geometrical constraints (cell dimensions, space group symmetry and heavy-atom locations) reducing the accessible conformational space, it is hoped that the absence of a well parametrized Ag^I force field affects only marginally the geometrical features of the structure.[3] Accordingly, we have minimized the steric energy of an Ag(im) chain in the crystalline lattice, with a local modification[3,34] of the MM3 program.[35] Our computations, showing that the experimental X-ray structure is very close to a steric energy minimum (root mean squared displacement 0.10 Å), further support the XRPD results. Of even higher importance, molecular mechanics has been used as a tool during the model formulation process, after having located the silver atoms in the cell. Since Fourier-difference methods from powder diffraction data might not succeed in locating unambiguously all missing atoms (particularly if they are separated by short interatomic distances), rough geometrical models can be built about the few observable peaks, and optimized by energy minimization within the crystal lattice to ensure a good starting point for a more reliable Rietveld least-squares refinement.

Again, we must emphasize that, while the refined, unrestrained distances involving light atoms might be fairly inaccurate, if compared to literature values, nevertheless the overall topology, conformation and crystal packing of the individual polymeric chains are well determined.

Conclusion

Fairly complex structures have been solved, and refined, from powder data by the combined use of high-flux, high-resolution sources, such as synchrotrons or time-of-flight neutrons, on classical inorganic compounds,[36] where the presence of tight ionic bonds increases both crystallinity and scattering power at high angles. However, despite (and thanks to) its complex features [i.e. the presence of two independent Ag(im) fragments, the non-centrosymmetric nature of the structure and the ambiguity of the systematic absences during the space group formulation process], this structure determination, as well as

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* For a quantomechanical interpretation of the nature of these weakly attractive interactions, see for example ref. 32(b).

those reported in refs. 3, 8, 9 and 10, raises the newly emerging technique[37] of *ab-initio* structure determination from X-ray powder diffraction data from its infancy to adolescence, by showing the viability of the powder method for obtaining structural information on moderately complex 'molecular' systems using conventional laboratory equipment.

Acknowledgements

References

1 M. Inoue and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1.
2 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497; S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115; P. J. Steel, *Coord. Chem. Rev.*, 1990, **106**, 227.
3 See, for example, N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, *J. Am. Chem. Soc.*, 1994, **116**, 7768, and refs. therein.
4 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2755.
5 G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi and M. Moret, *Inorg. Chem.*, 1994, **33**, 1458.
6 C. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293.
7 *Reviews in Mineralogy*, The Mineralogical Society of America, Washington, DC, 1989, vol. 20.
8 (*a*) K. Honda, M. Goto and M. Kurahashi, *Chem. Lett.*, 1990, 13; R. J. Cernik, A. K. Cheetham, C. K. Prout, D. J. Watkin, A. P. Wilkinson and B. T. M. Willis, *J. Appl. Crystallogr.*, 1991, **24**, 222; M. Kurahashi, *J. Crystallogr. Soc. Jpn*, 1992, **34**, 157; P. Lightfoot, M. Tremayne, K. D. M. Harris and P. G. Bruce, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1012; M. Tremayne, P. Lightfoot, C. Glidewell, K. D. M. Harris, K. Shankland, C. J. Gilmore, G. Bricogne and P. G. Bruce, *J. Mater. Chem.*, 1992, **2**, 1301; A. N. Fitch and J. K. Cockcroft, *Z. Kristallogr.*, 1992, **202**, 243 and refs. therein, (*b*) P. Lightfoot, C. Glidewell and P. G. Bruce, *J. Mater. Chem.*, 1992, **2**, 361; J. Fayos, G. Artioli and R. Torres, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 595; M. Baumgartner, H. Schmalle and C. Baerlocher, *J. Solid State Chem.*, 1993, **107**, 63; N. Masciocchi, P. Cairati, F. Ragaini and A. Sironi, *Organometallics*, 1993, **12**, 4499; S. Petit, G. Coquerel, G. Perez, D. Louer and M. Louer, *New J. Chem.*, 1993, **17**, 187; S. Petit, G. Coquerel, G. Perez, D. Louer and M. Louer, *Chem. Mater.*, 1994, **6**, 116.
9 N. Masciocchi, P. Cairati, L. Carlucci, G. Ciani, G. Mezza and A. Sironi, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3009.
10 N. Masciocchi, M. Moret, P. Cairati, F. Ragaini and A. Sironi, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 471.
11 H. F. Mc Murdie, M. Morris, E. Evans, B. Paretzkin and W. Wong-Ng, *Powder Diffr.*, 1986, **1**, 40.
12 P. E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Crystallogr.*, 1985, **18**, 367.
13 P. H. De Wolff, *J. Appl. Crystallogr.*, 1968, **1**, 108.
14 G. S. Smith and R. L. Snyder, *J. Appl. Crystallogr.*, 1979, **12**, 604.
15 G. S. Pawley, *J. Appl. Crystallogr.*, 1981, **14**, 357.
16 N. Masciocchi, R. Bianchi, P. Cairati, T. Pilati, G. Mezza and A. Sironi, *J. Appl. Crystallogr.*, 1994, **27**, 426.
17 A. C. Larson and R. B. Von Dreele, LANSCE, Ms-H805, Los Alamos National Laboratory, NM, 1990.
18 G. K. Wertheim, M. A. Butler, K. W. West and D. N. E. Buchanan, *Rev. Sci. Instrum.*, 1974, **45**, 1369.
19 G. Caglioti, A. Paoletti and F. P. Ricci, *Nucl. Instrum. Methods*, 1958, **3**, 223.
20 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79.
21 A. Z. March, *Z. Kristallogr.*, 1932, **81**, 285; W. A. Dollase, *J. Appl. Crystallogr.*, 1987, **19**, 267.
22 J. E. Bauman, jun. and J. C. Wang, *Inorg. Chem.*, 1964, **3**, 368.
23 G. Wyss, *Ber. Dtsch. Chem. Ges.*, 1877, **10**, 1365; E. Buchner, *Ber. Dtsch. Chem. Ges.*, 1889, **22**, 842.
24 C. Sigwart, P. Kroneck and P. Hemmerich, *Helv. Chim. Acta*, 1970, **53**, 177.
25 J. A. J. Jarvis and A. F. Wells, *Acta Crystallogr.*, 1960, **13**, 1027.
26 M. Sturm, F. Brandl, D. Engel and W. Hoppe, *Acta Crystallogr.*, *Sect. B*, 1975, **31**, 2369.
27 R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem.*, 1980, **464**, 187.
28 A. L. Spek, A. J. M. Duisenberg and M. C. Feiters, *Acta Crystallogr.*, *Sect. C*, 1983, **39**, 1212.
29 See, for example, J. Doucet, in *The Molecular Physics of Liquid Crystals*, eds. G. R. Luckhurst and G. W. Gray, Academic Press, London, 1979, ch. 14 and refs. therein.
30 B. Craven, R. K. McMullan, J. D. Bell and H. C. Freeman, *Acta Cystallogr.*, *Sect. B*, 1977, **33**, 2585.
31 M. Quiros, *Acta Crystallogr.*, *Sect. C*, 1994, **50**, 1236.
32 (*a*) M. Jansen, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 1098; (*b*) K. M. Merz, jun. and R. Hoffmann, *Inorg. Chem.*, 1988, **27**, 2120; (*c*) C. Koelmel and R. Ahlrichs, *J. Phys. Chem*, 1990, **94**, 5536 and refs. therein.
33 D. R. Ferro and S. Bruckner, *Macromolecules*, 1989, **22**, 2359.
34 M. Moret and A. Sironi, unpublished work.
35 N. L. Allinger, Y. H. Yuh and J. H. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8551.
36 See, for example, R. E. Morris, J. J. Owen, J. K. Stalick and A. K. Cheetham, *J. Solid State Chem.*, 1994, **111**, 52 and refs. therein.
37 F. G. Riddell, P. G. Bruce, P. Lightfoot and M. Rogerson, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 209.