

Material Supplementary for

Structural movies of the gradual spin-crossover in a molecular complex at various physical scales.

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A- Experimental and crystallographic data for the SCXRD study of [Fe(PM-AzA)₂(NCS)₂]

B- Experimental and crystallographic data for the SCXRD study of [Zn(PM-AzA)₂(NCS)₂]

C- MOSSBAUER of [Fe(PM-AzA)₂(NCS)₂]

D- Matrix of the DILATATION TENSORS

E- POSITIONNAL DISORDER in [Fe(PM-AzA)₂(NCS)₂]

F- Structural movies: see attached .ppt file

A- Experimental and crystallographic data for the SCXRD study of [Fe(PM-AzA)₂(NCS)₂]

| T(K) | 290 | 270 | 250 | 230 | 210 | 190 | 170 | 150 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,1215(12) | 15,1117(11) | 15,1063(11) | 15,0961(11) | 15,0821(11) | 15,0573(10) | 15,0294(11) | 15,0119(11) |
| b (Å) | 14,5537(12) | 14,5148(12) | 14,4809(11) | 14,4493(11) | 14,4302(11) | 14,4200(10) | 14,4106(11) | 14,3903(11) |
| c (Å) | 17,0259(8) | 17,0110(8) | 16,9914(8) | 16,9550(7) | 16,8916(7) | 16,7947(7) | 16,7098(7) | 16,6678(8) |
| β (°) | 92,957(4) | 93,032(4) | 93,085(4) | 93,099(4) | 93,026(4) | 92,889(4) | 92,796(4) | 92,793(4) |
| V (Å ³) | 3742,0(5) | 3726,0(4) | 3711,5(4) | 3693,0(4) | 3671,1(4) | 3641,9(4) | 3614,7(4) | 3596,4(4) |
| μ (mm ⁻¹) | 0,556 | 0,559 | 0,561 | 0,564 | 0,567 | 0,572 | 0,576 | 0,579 |
| ρ (g cm ⁻³) | 1,322 | 1,327 | 1,333 | 1,339 | 1,347 | 1,358 | 1,368 | 1,375 |
| Domaine angulaire θ (°) | 2,25 – 22,98 | 2,25 – 21,25 | 2,25 – 21,24 | 2,25 – 21,31 | 2,26 - 21,24 | 3,34 - 21,25 | 3,34 - 21,25 | 3,35 - 21,25 |
| Complétude | 0,75 | 0,85 | 0,85 | 0,84 | 0,85 | 0,85 | 0,85 | 0,85 |
| h min / max | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 |
| k min / max | -12/14 | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 |
| l min / max | -14/13 | -14/13 | -14/13 | -14/13 | -14/13 | -14/13 | -13/13 | -13/13 |
| Réflexions collectées | 6377 | 5885 | 5852 | 5827 | 5776 | 5754 | 5700 | 5650 |
| Réflexions Indépendantes (R _{int}) | 3871 (0,0273) | 3509 (0,0250) | 3493 (0,0239) | 3484 (0,0231) | 3449 (0,0233) | 3434 (0,0219) | 3408 (0,0215) | 3378 (0,0208) |
| R(sigma) | 0,0475 | 0,0428 | 0,0417 | 0,0407 | 0,0400 | 0,0389 | 0,0380 | 0,0367 |
| Réflexions Observées seuil : I/σ(I)=2 | 2882 | 2759 | 2769 | 2809 | 2824 | 2862 | 2929 | 2956 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R _{obs} (all) | 0,0401 (0,0633) | 0,0371 (0,0545) | 0,0353 (0,0517) | 0,0350 (0,0496) | 0,0340 (0,0469) | 0,0326 (0,0443) | 0,0298 (0,0387) | 0,0273 (0,0348) |
| wR ₂ _{obs} (all) | 0,0806 (0,0897) | 0,0784 (0,0860) | 0,0773 (0,0847) | 0,0778 (0,0847) | 0,0778 (0,0840) | 0,0748 (0,0806) | 0,0700 (0,0743) | 0,0651 (0,0689) |
| S | 1,042 | 1,046 | 1,050 | 1,032 | 1,028 | 1,060 | 1,025 | 1,012 |
| Δρ _{min} / Δρ _{max} (e ⁻ · Å ⁻³) | -0,150/0,289 | 0,305/-0,178 | 0,278/-0,167 | 0,262/-0,206 | 0,241/-0,209 | 0,270/-0,207 | 0,294/-0,183 | 0,248/-0,175 |

| T(K) | 130 | 110 | 140 | 160 | 180 | 200 | 220 | 240 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,0090(11) | 14,9984(9) | 15,0070(10) | 15,0178(10) | 15,0406(10) | 15,0713(10) | 15,0861(11) | 15,1046(11) |
| b (Å) | 14,3641(11) | 14,3524(10) | 14,3798(10) | 14,4001(10) | 14,4132(10) | 14,4223(11) | 14,4369(11) | 14,4631(11) |
| c (Å) | 16,6475(7) | 16,6350(6) | 16,6543(6) | 16,6809(7) | 16,7432(7) | 16,8453(7) | 16,9270(7) | 16,9754(8) |
| β (°) | 92,803(4) | 92,822(3) | 92,812(3) | 92,794(4) | 92,832(3) | 92,962(4) | 93,073(4) | 93,103(4) |
| V (Å ³) | 3584,8(4) | 3576,6(4) | 3589,6(4) | 3603,1(4) | 3625,2(4) | 3656,6(4) | 3681,3(4) | 3703,0(4) |
| μ (mm ⁻¹) | 0,581 | 0,582 | 0,580 | 0,578 | 0,574 | 0,569 | 0,565 | 0,562 |
| ρ (g cm ⁻³) | 1,380 | 1,383 | 1,378 | 1,373 | 1,364 | 1,353 | 1,344 | 1,336 |
| Domaine angulaire θ (°) | 3,35 - 21,28 | 3,35 - 21,27 | 3,35 - 21,30 | 2,28 - 21,28 | 3,34 - 21,26 | 2,26 - 21,23 | 2,26 - 21,27 | 2,25 - 21,23 |
| Complétude | 0,84 | 0,85 | 0,84 | 0,85 | 0,85 | 0,85 | 0,85 | 0,85 |
| h min / max | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 |
| k min / max | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 | -11/14 |
| l min / max | -13/13 | -13/13 | -13/13 | -13/13 | -14/13 | -14/13 | -14/13 | -14/13 |
| Réflexions collectées | 5624 | 5635 | 5659 | 5688 | 5728 | 5753 | 5805 | 5833 |
| Réflexions Indépendantes (R_{int}) | 3376 (0,0212) | 3366 (0,0262) | 3382 (0,0197) | 3396 (0,0200) | 3416 (0,0220) | 3432 (0,0232) | 3470 (0,0236) | 3476 (0,0240) |
| R(sigma) | 0,0363 | 0,0384 | 0,0357 | 0,0365 | 0,0381 | 0,0398 | 0,0405 | 0,0413 |
| Réflexions Observées seuil : $I/\sigma(I)=2$ | 2986 | 3007 | 2985 | 2941 | 2882 | 2822 | 2810 | 2767 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R_{obs} (all) | 0,0263 (0,0328) | 0,0277 (0,0332) | 0,0265 (0,0328) | 0,0285 (0,0366) | 0,0306 (0,0412) | 0,0329 (0,0453) | 0,0339 (0,0476) | 0,0351 (0,0503) |
| $wR2_{obs}$ (all) | 0,0619 (0,0650) | 0,0661 (0,0689) | 0,0606 (0,0634) | 0,0653 (0,0695) | 0,0697 (0,0749) | 0,0744 (0,0802) | 0,0749 (0,0809) | 0,0775 (0,0841) |
| S | 1,033 | 1,040 | 1,049 | 1,041 | 1,030 | 1,048 | 1,044 | 1,051 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ (e ⁻ · Å ⁻³) | 0,164/-0,186 | 0,192/-0,215 | 0,186/-0,176 | 0,263/-0,193 | 0,280/-0,196 | 0,262/-0,196 | 0,275/-0,209 | 0,267/-0,184 |

| T(K) | 260 | 280 | 290 | 285 | 265 | 245 | 225 | 205 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,1103(11) | 15,1186(12) | 15,1213(7) | 15,1196(7) | 15,1158(7) | 15,1081(7) | 15,0984(6) | 15,0800(7) |
| b (Å) | 14,4939(12) | 14,5293(12) | 14,5553(10) | 14,5444(10) | 14,5070(9) | 14,4721(9) | 14,4452(9) | 14,4253(9) |
| c (Å) | 17,0017(8) | 17,0171(8) | 17,0282(11) | 17,0230(11) | 17,0102(11) | 16,9844(11) | 16,9444(10) | 16,8673(11) |
| β (°) | 93,063(4) | 93,012(4) | 92,945(4) | 92,966(4) | 93,051(4) | 93,095(4) | 93,086(3) | 92,994(3) |
| V (Å ³) | 3718,2(4) | 3732,9(5) | 3742,9(4) | 3738,4(4) | 3724,8(4) | 3708,2(4) | 3690,2(3) | 664,2(4) |
| μ (mm ⁻¹) | 0,560 | 0,558 | 0,556 | 0,557 | 0,559 | 0,561 | 0,564 | 0,568 |
| ρ (g cm ⁻³) | 1,330 | 1,325 | 1,322 | 1,323 | 1,328 | 1,334 | 1,340 | 1,350 |
| Domaine angulaire θ (°) | 2,25 - 21,26 | 2,25 - 21,25 | 2,25 - 21,27 | 2,25 - 21,26 | 2,25 - 21,26 | 2,25 - 21,26 | 2,26 - 21,25 | 3,33 - 21,25 |
| Complétude | 0,85 | 0,85 | 0,92 | 0,92 | 0,91 | 0,91 | 0,92 | 0,92 |
| h min / max | -15/15 | -15/15 | -15/14 | -15/14 | -14/14 | -14/14 | -14/14 | -14/14 |
| k min / max | -11/14 | -11/14 | -15/14 | -15/14 | -14/11 | -14/11 | -14/11 | -14/11 |
| l min / max | -14/13 | -14/13 | -17/17 | -17/17 | -17/17 | -17/17 | -17/17 | -17/17 |
| Réflexions collectées | 5872 | 5876 | 5484 | 5476 | 5453 | 5431 | 5402 | 5359 |
| Réflexions Indépendantes (R_{int}) | 3506 (0,0247) | 3507 (0,0251) | 3816 (0,0236) | 3810 (0,0234) | 3791 (0,0234) | 3776 (0,0231) | 3759 (0,0224) | 3732 (0,0230) |
| R(sigma) | 0,0424 | 0,0433 | 0,0451 | 0,0451 | 0,0438 | 0,0426 | 0,0417 | 0,0416 |
| Réflexions Observées seuil : $I/\sigma(I)=2$ | 2763 | 2745 | 2977 | 2988 | 2995 | 3035 | 3069 | 3074 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R_{obs} (all) | 0,0364 (0,0532) | 0,0373 (0,0554) | 0,0375 (0,0548) | 0,0379 (0,0561) | 0,0360 (0,0530) | 0,0359 (0,0511) | 0,0349 (0,0488) | 0,0343 (0,0472) |
| $wR2_{obs}$ (all) | 0,0796 (0,0869) | 0,0763 (0,0843) | 0,0807 (0,0888) | 0,0789 (0,0869) | 0,0794 (0,0874) | 0,0766 (0,0843) | 0,0750 (0,0818) | 0,0749 (0,0814) |
| S | 1,047 | 1,051 | 1,029 | 1,037 | 1,037 | 1,042 | 1,035 | 1,034 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ (e ⁻ · Å ⁻³) | 0,287/-0,187 | 0,286/-0,148 | 0,201/-0,162 | 0,210/-0,164 | 0,217/-0,185 | 0,213/-0,183 | 0,267/-0,191 | 0,265/-0,218 |

| T(K) | 185 | 165 | 145 | 125 | 105 | 115 | 135 | 155 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,0534(8) | 15,0266(8) | 15,0133(8) | 15,0070(8) | 15,0064(8) | 15,0068(9) | 15,0091(9) | 15,0171(9) |
| b (Å) | 14,4184(10) | 14,4078(11) | 14,3893(11) | 14,3657(10) | 14,3397(11) | 14,3500(12) | 14,3725(12) | 14,3939(12) |
| c (Å) | 16,7682(12) | 16,6985(13) | 16,6664(12) | 16,6511(12) | 16,6293(13) | 16,6364(14) | 16,6495(14) | 16,6705(14) |
| β (°) | 92,865(4) | 92,813(4) | 92,825(4) | 92,856(4) | 92,918(5) | 92,859(5) | 92,839(5) | 92,807(5) |
| V (Å ³) | 3634,9(4) | 3610,9(4) | 3596,1(4) | 3585,3(4) | 3573,8(4) | 3578,1(5) | 3587,2(5) | 3599,1(5) |
| μ (mm ⁻¹) | 0,573 | 0,577 | 0,579 | 0,581 | 0,583 | 0,582 | 0,580 | 0,578 |
| ρ (g cm ⁻³) | 1,361 | 1,370 | 1,375 | 1,380 | 1,384 | 1,382 | 1,379 | 1,374 |
| Domaine angulaire θ (°) | 3,34 - 22,97 | 3,34 - 22,97 | 3,35 - 22,97 | 3,35 - 22,96 | 3,36 - 22,97 | 3,35 - 23,00 | 3,35 - 22,99 | 3,35 - 22,97 |
| Complétude | 0,81 | 0,81 | 0,81 | 0,81 | 0,80 | 0,80 | 0,80 | 0,80 |
| h min / max | -15/14 | -15/14 | -15/14 | -15/14 | -15/14 | -15/14 | -15/14 | -15/14 |
| k min / max | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 |
| l min / max | -18/18 | -18/17 | -18/17 | -18/17 | -18/17 | -18/17 | -18/17 | -18/17 |
| Réflexions collectées | 5705 | 5651 | 5636 | 5597 | 5527 | 5529 | 5543 | 5570 |
| Réflexions Indépendantes (R_{int}) | 4090 (0,0226) | 4057 (0,0242) | 4035 (0,0242) | 4010 (0,0245) | 3981 (0,0237) | 3980 (0,0263) | 3987 (0,0262) | 4005 (0,0259) |
| R(sigma) | 0,0425 | 0,0420 | 0,0415 | 0,0410 | 0,0408 | 0,0424 | 0,0429 | 0,0437 |
| Réflexions Observées seuil : $I/\sigma(I)=2$ | 3346 | 3443 | 3489 | 3482 | 3481 | 3441 | 3440 | 3411 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R_{obs} (all) | 0,0358 (0,0486) | 0,0333 (0,0428) | 0,0306 (0,0390) | 0,0292 (0,0374) | 0,0286 (0,0359) | 0,0302 (0,0386) | 0,0301 (0,0386) | 0,0327 (0,0427) |
| $wR2_{obs}$ (all) | 0,0791 (0,0854) | 0,0746 (0,0793) | 0,0678 (0,0715) | 0,0659 (0,0699) | 0,0661 (0,0697) | 0,0702 (0,0744) | 0,0682 (0,0725) | 0,0727 (0,0773) |
| S | 1,023 | 1,028 | 1,026 | 1,026 | 1,022 | 1,030 | 1,015 | 1,026 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ (e ⁻ · Å ⁻³) | 0,423/-0,208 | 0,404/-0,209 | 0,328/-0,193 | 0,216/-0,204 | 0,221/-0,233 | 0,253/-0,236 | 0,274/-0,258 | 0,341/-0,229 |

| T(K) | 175 | 195 | 215 | 235 | 255 | 275 | 295 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,0368(9) | 15,0676(7) | 15,0902(6) | 15,1045(7) | 15,1127(7) | 15,1192(7) | 15,1239(7) |
| b (Å) | 14,4119(12) | 14,4217(10) | 14,4342(9) | 14,4584(9) | 14,4897(9) | 14,5268(9) | 14,5665(10) |
| c (Å) | 16,7208(14) | 16,8187(11) | 16,9112(10) | 16,9678(10) | 16,9969(10) | 17,0178(10) | 17,0273(11) |
| β (°) | 92,815(5) | 92,929(4) | 93,056(3) | 93,103(4) | 93,083(4) | 93,017(4) | 92,929(4) |
| V (Å ³) | 3619,2(5) | 3649,9(4) | 3678,3(3) | 3700,1(4) | 3716,6(4) | 3732,5(4) | 3746,3(4) |
| μ (mm ⁻¹) | 0,575 | 0,570 | 0,566 | 0,563 | 0,560 | 0,558 | 0,556 |
| ρ (g cm ⁻³) | 1,367 | 1,355 | 1,345 | 1,337 | 1,331 | 1,325 | 1,320 |
| Domaine angulaire θ (°) | 3,34 – 22,98 | 3,33 - 22,98 | 2,26 - 22,97 | 2,25 - 22,97 | 2,25 - 22,98 | 2,25 - 22,97 | 2,25 - 22,98 |
| Complétude | 0,80 | 0,81 | 0,82 | 0,82 | 0,81 | 0,82 | 0,81 |
| h min / max | -15/14 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 | -15/15 |
| k min / max | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 | -15/11 |
| l min / max | -18/18 | -18/18 | -18/18 | -18/18 | -18/18 | -18/18 | -18/18 |
| Réflexions collectées | 5633 | 5767 | 5827 | 5859 | 5886 | 5903 | 5918 |
| Réflexions Indépendantes (R_{int}) | 4041 (0,0249) | 4121 (0,0236) | 4163 (0,0229) | 4181 (0,0227) | 4201 (0,0233) | 4214 (0,0235) | 4228 (0,0233) |
| R(sigma) | 0,0437 | 0,0443 | 0,0442 | 0,0449 | 0,0462 | 0,0474 | 0,0487 |
| Réflexions Observées seuil : $I/\sigma(I)=2$ | 3343 | 3312 | 3303 | 3289 | 3244 | 3217 | 3159 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R_{obs} (all) | 0,0348 (0,0469) | 0,0365 (0,0512) | 0,0381 (0,0539) | 0,0393 (0,0566) | 0,0389 (0,0584) | 0,0403 (0,0618) | 0,0421 (0,0657) |
| $wR2_{obs}$ (all) | 0,0773 (0,0832) | 0,0779 (0,0848) | 0,0797 (0,0872) | 0,0798 (0,0873) | 0,0801 (0,0895) | 0,0810 (0,0906) | 0,0822 (0,0920) |
| S | 1,047 | 1,024 | 1,039 | 1,043 | 1,038 | 1,025 | 1,032 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ (e ⁻ · Å ⁻³) | 0,444/-0,225 | 0,394/-0,213 | 0,337/-0,219 | 0,275/ -0,204 | 0,292/-0,197 | 0,256/-0,185 | 0,231/-0,175 |

B- Experimental and crystallographic data for the SCXRD study of [Zn(PM-AzA)₂(NCS)₂]

| T(K) | 290 | 270 | 250 | 230 | 210 | 190 | 170 | 150 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,1300(8) | 15,1251(8) | 15,1195(7) | 15,1135(7) | 15,1082(7) | 15,1034(6) | 15,0995(6) | 15,0958(6) |
| b (Å) | 14,5806(13) | 14,5335(12) | 14,4879(11) | 14,4437(10) | 14,4006(10) | 14,3594(10) | 14,3215(10) | 14,2842(9) |
| c (Å) | 17,1485(16) | 17,1467(15) | 17,1458(13) | 17,1447(12) | 17,1451(12) | 17,1456(11) | 17,1475(11) | 17,1476(11) |
| β (°) | 93,558(5) | 93,657(5) | 93,756(4) | 93,836(4) | 93,924(4) | 94,006(4) | 94,087(4) | 94,159(3) |
| V (Å ³) | 3775,7(5) | 3761,5(5) | 3747,7(4) | 3734,2(4) | 3721,5(4) | 3709,4(4) | 3698,7(4) | 3687,8(4) |
| μ (mm ⁻¹) | 0,802 | 0,805 | 0,808 | 0,811 | 0,814 | 0,817 | 0,819 | 0,822 |
| ρ (g cm ⁻³) | 1,327 | 1,332 | 1,337 | 1,342 | 1,346 | 1,350 | 1,354 | 1,358 |
| Domaine angulaire θ (°) | 2,23 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,25 – 25,04 |
| Complétude | 0,75 | 0,75 | 0,73 | 0,75 | 0,74 | 0,74 | 0,74 | 0,74 |
| h min / max | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 |
| k min / max | -10/16 | -10/16 | -10/16 | -10/16 | -10/16 | -10/16 | -10/16 | -10/15 |
| l min / max | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 |
| Réflexions collectées | 6496 | 6447 | 6247 | 6364 | 6349 | 6307 | 6270 | 6255 |
| Réflexions Indépendantes (R _{int}) | 4961 (0,0256) | 4954 (0,0214) | 4853 (0,0373) | 4904 (0,0171) | 4893 (0,0171) | 4856 (0,0164) | 4832 (0,0170) | 4823 (0,0165) |
| R(sigma) | 0,0515 | 0,0486 | 0,0467 | 0,0377 | 0,0371 | 0,0364 | 0,0361 | 0,0354 |
| Réflexions Observées seuil : I/σ(I)=2 | 3519 | 3678 | 3908 | 4098 | 4170 | 4213 | 4246 | 4326 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R _{obs} (all) | 0,0504 (0,0806) | 0,0501 (0,0743) | 0,0571 (0,0720) | 0,0475 (0,0589) | 0,0477 (0,0579) | 0,0464 (0,0548) | 0,0450 (0,0524) | 0,0437 (0,0497) |
| wR2 _{obs} (all) | 0,1164 (0,1323) | 0,1238 (0,1370) | 0,1567 (0,1690) | 0,1253 (0,1330) | 0,1269 (0,1341) | 0,1233 (0,1292) | 0,1193 (0,1245) | 0,1169 (0,1212) |
| S | 1,044 | 1,033 | 1,054 | 1,048 | 1,064 | 1,058 | 1,050 | 1,067 |
| Δρ _{min} / Δρ _{max} (e ⁻ · Å ⁻³) | -0,247/0,559 | -0,219/0,706 | -0,307/0,880 | -0,278/0,950 | -0,316/1,107 | -0,305/1,197 | -0,249/1,327 | -0,253/1,457 |

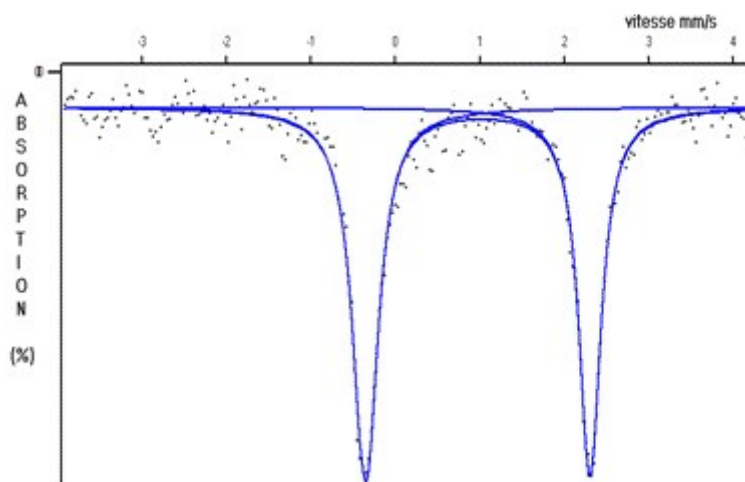
| T(K) | 130 | 110 | 90 | 100 | 120 | 140 | 160 | 180 |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,0934(6) | 15,0918(6) | 15,0920(6) | 15,0917(6) | 15,0920(6) | 15,0940(6) | 15,0970(6) | 15,1007(6) |
| b (Å) | 14,2495(9) | 14,2146(9) | 14,1832(9) | 14,1960(9) | 14,2288(9) | 14,2636(9) | 14,3013(9) | 14,3389(10) |
| c (Å) | 17,1470(10) | 17,1441(10) | 17,1387(10) | 17,1443(10) | 17,1508(10) | 17,1499(11) | 17,1496(11) | 17,1477(11) |
| β (°) | 94,234(3) | 94,286(3) | 94,321(3) | 94,310(3) | 94,277(3) | 94,206(3) | 94,136(4) | 94,055(4) |
| V (Å ³) | 3677,8(3) | 3667,5(3) | 3658,2(3) | 3662,6(3) | 3672,7(3) | 3682,3(4) | 3693,1(4) | 3703,7(4) |
| μ (mm ⁻¹) | 0,824 | 0,826 | 0,828 | 0,827 | 0,825 | 0,823 | 0,820 | 0,818 |
| ρ (g cm ⁻³) | 1,362 | 1,366 | 1,369 | 1,368 | 1,364 | 1,360 | 1,356 | 1,353 |
| Domaine angulaire θ (°) | 2,23 – 25,02 | 2,25 – 25,03 | 2,24 – 25,02 | 2,25 – 25,02 | 2,25 – 25,04 | 2,25 – 25,03 | 2,25 – 25,02 | 2,24 – 25,02 |
| Complétude | 0,74 | 0,74 | 0,74 | 0,74 | 0,74 | 0,74 | 0,74 | 0,74 |
| h min / max | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 |
| k min / max | -10/15 | -10/15 | -10/15 | -10/15 | -10/15 | -10/15 | -10/15 | -10/16 |
| l min / max | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 |
| Réflexions collectées | 6234 | 6199 | 6201 | 6214 | 6194 | 6207 | 6250 | 6271 |
| Réflexions Indépendantes (R_{int}) | 4801 (0,0170) | 4780 (0,0167) | 4782 (0,0168) | 4779 (0,0168) | 4793 (0,0164) | 4805 (0,0169) | 4824 (0,0170) | 4832 (0,0170) |
| R(sigma) | 0,0349 | 0,0345 | 0,0343 | 0,0345 | 0,0347 | 0,0353 | 0,0358 | 0,0363 |
| Réflexions Observées seuil : $I/\sigma(I)=2$ | 4389 | 4413 | 4457 | 4423 | 4404 | 4326 | 4274 | 4218 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 | 460 | 460 | 460 |
| R_{obs} (all) | 0,0430 (0,0481) | 0,0423 (0,0463) | 0,0423 (0,0455) | 0,0421 (0,0458) | 0,0422 (0,0465) | 0,0431 (0,0488) | 0,0446 (0,0513) | 0,0458 (0,0539) |
| $wR2_{obs}$ (all) | 0,1131 (0,1167) | 0,1044 (0,1069) | 0,1068 (0,1088) | 0,1076 (0,1100) | 0,1077 (0,1105) | 0,1083 (0,1119) | 0,1185 (0,1234) | 0,1174 (0,1228) |
| S | 1,085 | 1,060 | 1,077 | 1,075 | 1,087 | 1,060 | 1,053 | 1,030 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ (e ⁻ · Å ⁻³) | -0,326/1,646 | -0,303/1,759 | -0,310/ 1,896 | -0,284/ 1,874 | -0,257/ 1,673 | -0,277/ 1,563 | -0,260/ 1,401 | -0,274/ 1,233 |

| T(K) | 200 | 220 | 240 | 260 | 280 |
|--|--------------------|--------------------|--------------------|--------------------|--------------------|
| a (Å) | 15,1058(7) | 15,1104(7) | 15,1170(7) | 15,1221(7) | 15,1281(7) |
| b (Å) | 14,3790(10) | 14,4217(10) | 14,4666(10) | 14,5091(11) | 14,5550(11) |
| c (Å) | 17,1457(12) | 17,1457(12) | 17,1452(12) | 17,1448(13) | 17,1464(13) |
| β (°) | 93,973(4) | 93,883(4) | 93,793(4) | 93,707(4) | 93,621(4) |
| V (Å ³) | 3715,2(4) | 3727,8(4) | 3741,3(4) | 3753,8(4) | 3767,9(4) |
| μ (mm ⁻¹) | 0,816 | 0,813 | 0,810 | 0,807 | 0,804 |
| ρ (g cm ⁻³) | 1,348 | 1,344 | 1,339 | 1,334 | 1,330 |
| Domaine angulaire θ (°) | 2,24 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,24 – 25,02 | 2,23 – 25,02 |
| Complétude | 0,74 | 0,74 | 0,74 | 0,74 | 0,74 |
| h min / max | -13/14 | -13/14 | -13/14 | -13/14 | -13/14 |
| k min / max | -10/16 | -10/16 | -10/16 | -10/16 | -10/16 |
| l min / max | -20/20 | -20/20 | -20/20 | -20/20 | -20/20 |
| Réflexions collectées | 6282 | 6360 | 6329 | 6395 | 6403 |
| Réflexions Indépendantes (R_{int}) | 4853 (0,0168) | 4875 (0,0196) | 4894 (0,0168) | 4922 (0,0170) | 4932 (0,0172) |
| R (sigma) | 0,0368 | 0,0368 | 0,0387 | 0,0389 | 0,0397 |
| Réflexions Observées seuil : I / σ (I)=2 | 4155 | 4094 | 4017 | 3973 | 3891 |
| Nombre de paramètres | 460 | 460 | 460 | 460 | 460 |
| R_{obs} (all) | 0,0467 (0,0558) | 0,0468 (0,0585) | 0,0476 (0,0604) | 0,0484 (0,0635) | 0,0468 (0,0635) |
| wR_{2obs} (all) | 0,1203 (0,1265) | 0,1160 (0,1240) | 0,1239 (0,1329) | 0,1251 (0,1352) | 0,1132 (0,1231) |
| S | 1,057 | 1,046 | 1,044 | 1,071 | 1,035 |
| Δρ_{min}/Δρ_{max} (e ⁻ · Å ⁻³) | -0,273/1,121 | -0,293/1,016 | -0,251/0,846 | -0,247/0,762 | -0,244/0,579 |

| T(K) | 80 | 290 |
|--|----------------------------------|---------------|
| Dimensions du cristal (mm ³) | 0,6 x 0,6 x 0,45 mm ³ | |
| Système | monoclinique | |
| Groupe d'espace | P 2 ₁ /c, Z=4 | |
| <u>a</u> (Å) | 15,0997(2) | 15,1376(3) |
| <u>b</u> (Å) | 14,1762(2) | 14,5802(3) |
| <u>c</u> (Å) | 17,1299(3) | 17,1465(4) |
| β (°) | 94,3202(9) | 93,5485(13) |
| V (Å ³) | 3656,4(1) | 3777,2(2) |
| mosaïcité (°) | 0,882(1) | 0,905(1) |
| absorption μ (mm ⁻¹) | 0,83 | 0,80 |
| Domaine angulaire θ (°) | 2,25 / 30,04 | 2,23 / 30,05 |
| Complétude | 0,997 | 0,998 |
| h min / max | -21/21 | -21/21 |
| k min / max | -19/19 | -20/20 |
| l min / max | -24/24 | -24/24 |
| Réflexions collectées | 21321 | 22045 |
| Réflexions Indépendantes (R _{int}) | 10671 (0,015) | 11045 (0,028) |
| R(sigma) | 0,022 | 0,036 |
| Réflexions Observées (I/ σ (I) \geq 2) | 9651 | 6605 |
| Nombre de paramètres affinés | 460 | 460 |
| R _{obs} (all) | 0,043(0,049) | 0,058(0,103) |
| wR2 _{obs} (all) | 0,1185 | 0,184 |
| S | 1,07 | 1,03 |
| $\Delta\rho_{\max} / \Delta\rho_{\min}$ (e ⁻ ·Å ⁻³) | 3,16/ -0,33 | 0,85/-0,51 |

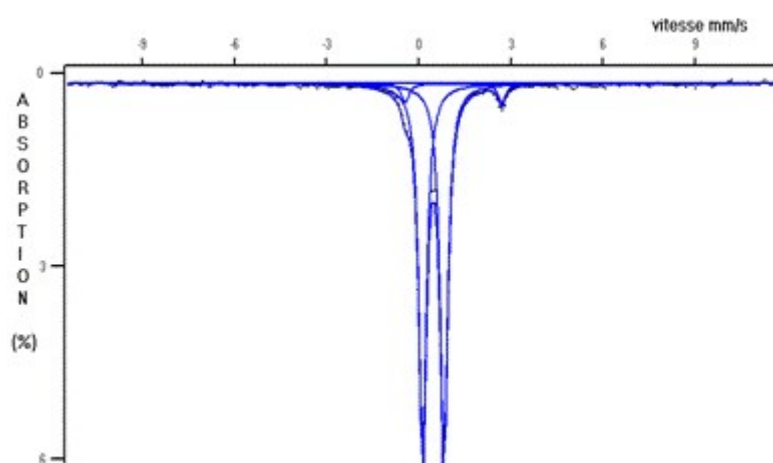
C- MOSSBAUER of $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$

At 295 K



| Site | δ (mm/s) | Γ (mm/s) | Δ (mm/s) | % | |
|------|-----------------|-----------------|-----------------|-------|---------------------|
| 1 | 0,96 | 0,34 | 2,66 | 100,0 | Fe^{2+} HS |

At 4.2K



| Site | δ (mm/s) | Γ (mm/s) | Δ (mm/s) | % |
|------|-----------------|-----------------|-----------------|----|
| 1 | 1,1 | 0,27 | 3,1 | 5 |
| 2 | 0,43 | 0,30 | 0,70 | 95 |

D- Matrix of the DILATATION TENSORS

PAScal software.



In the range [295-260 K]

| | <u>a</u> | <u>b</u> | <u>c</u> | α (10 ⁻⁶ K ⁻¹) |
|----|----------|----------|----------|--|
| X1 | 0,8811 | 0,0000 | -0,4728 | -9(8) |
| X2 | 0,5824 | 0,0000 | 0,8129 | 56(13) |
| X3 | 0,0000 | 1,0000 | 0,0000 | 120(14) |
| V | | | | 222(24) |



In the range [140-105 K]

| | <u>a</u> | <u>b</u> | <u>c</u> | α (10 ⁻⁶ K ⁻¹) |
|----|----------|----------|----------|--|
| X1 | 0,9545 | 0,0000 | -0,2983 | 4 (10) |
| X2 | 0,3970 | 0,0000 | 0,9178 | 50(7) |
| X3 | 0,0000 | 1,0000 | 0,0000 | 72(6) |
| V | | | | 129(5) |



In the range [295-260 K]

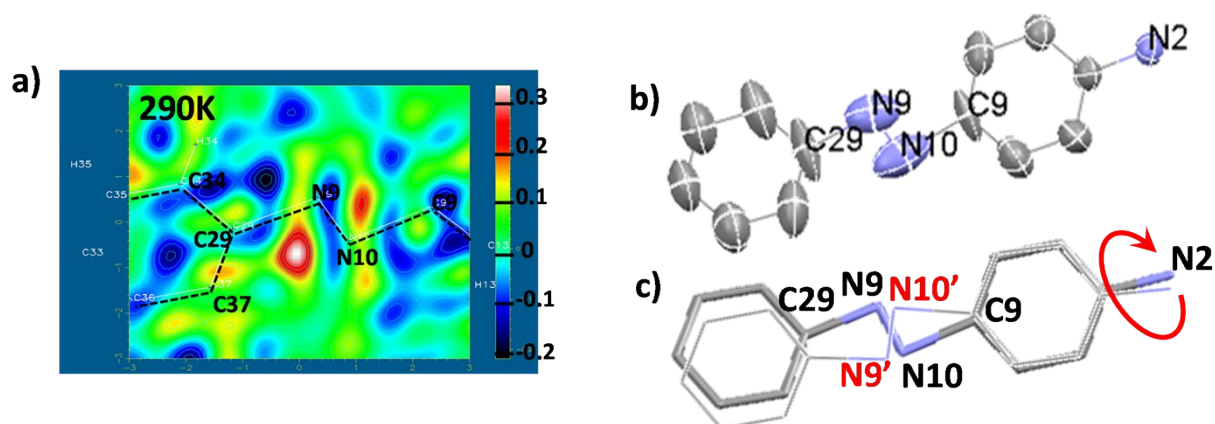
| | <u>a</u> | <u>b</u> | <u>c</u> | α (10 ⁻⁶ K ⁻¹) |
|----|----------|----------|----------|--|
| X1 | 0,6839 | 0,0000 | -0,7295 | -28(2) |
| X2 | 0,8014 | 0,0000 | 0,5982 | 58(1) |
| X3 | 0,0000 | -1,0000 | 0,0000 | 164(1) |
| V | | | | 194(2) |



In the range [140-100 K]

| Axes principaux | <u>a</u> | <u>b</u> | <u>c</u> | α (10 ⁻⁶ K ⁻¹) |
|-----------------|----------|----------|----------|--|
| X1 | 0,8995 | 0,0000 | -0,4369 | -15(1) |
| X2 | 0,5645 | 0,0000 | 0,8254 | 31(1) |
| X3 | 0,0000 | 1,0000 | 0,0000 | 119(2) |
| V | | | | 135(1) |

E- POSITIONAL DISORDER in $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$



A) Difference Fourier map showing the positional disorder in the PM-AzA ligand

B) View of ADP when the main positions are used

C) Representation of the disorder, structural data as collected here (0.9 Å resolution) does not allow to refine the secondary positions