

TABLE V. Mössbauer parameters for FePc and FePc (treated).

Pressure (kbar)	Isomer shift (mm/sec) ^a							
	0	25	50	70	100	125	150	175
Starting material								
FePc	0.385	0.373	0.350	0.328	0.302	0.290	0.280	0.274
FePc (heated in 2-picoline)	0.290	0.170	0.126	0.125	0.138	0.158	0.165	0.165
FePc (heated in air)	0.348	0.353	0.361	0.380	0.400	0.413	0.425	0.436
FePc (sheared)	0.353	0.435
High pressure material								
FePc	0.385	0.373	0.350	0.328	0.302	0.290	0.280	0.274
FePc (heated in 2-picoline)	0.360	0.295	0.235	0.220	0.210	0.210
FePc (heated in air)	0.390	0.400	0.400	0.397	0.395	0.394
FePc (sheared)	0.416
Quadrupole splitting (mm/sec)								
Starting material								
FePc	2.58	2.74	2.90	3.03	3.14	3.18	3.21	3.23
FePc (heated in 2-picoline)	0.36	1.09	1.62	1.81	1.98	2.06	2.14	2.18
FePc (heated in air)	1.13	1.24	1.30	1.33	1.37	1.41	1.45	1.49
FePc (sheared)	0.71	1.23
High pressure material								
FePc	2.58	2.74	2.90	3.03	3.14	3.18	3.21	3.23
FePc (heated in 2-picoline)	3.01	3.13	3.23	3.28	3.31	3.33
FePc (heated in air)	2.82	2.99	3.09	3.14	3.18	3.22
FePc (sheared)	2.94
Pressure (kbar)								
	50	70	90	110	130	150	175	
FePc (heated in 2-picoline)	32.5	51.0	57.5	60.5	61.5	62.0	62.5	
FePc (heated in air)	42.0	46.5	48.2	49.1	49.2	49.2	49.2	
FePc (sheared)	...	56.0	

^a Relative to iron metal.

appeared to give a spectrum similar to the normal FePc spectrum. Upon release of pressure the original spectrum reappeared. In FePc (heated in 2-picoline), pressure appeared to cause a change in spin state analogous to the change which occurred in the pyridine and picoline adducts of FePc. The original low spin material has an isomer shift similar to the low spin FePc complexes given in Table II. Its quadrupole splitting shows a very large increase, up to the magnitude of the other low spin complexes (Table II). Upon release of pressure the original spectrum reappeared, with some hysteresis present. The percent conversions to high pressure material are compared in Table V.

Since the high pressure Mössbauer apparatus involves nonhydrostatic media, a question arises concerning the amount of shear exerted on the sample. As FePc is very sensitive to shear and the sheared material has a distinctive Mössbauer spectrum, it provides a good test. With increasing pressure we observed only a change

of isomer shift and quadrupole splitting—at no pressure could there have been more than 5%–10% shear product present. Where the pressure was released to 1 atm, significant amounts of shear product (sometimes as much as 25%–30%) were observed. Apparently with increasing pressure there is very little shear, which would indicate a small pressure gradient, while during release there is a considerable gradient and measurable shear. This is consistent with other observations we have made. With the substituted phthalocyanines there was no evidence of any shear effects with increasing pressure. There could have been a few percent (less than 10) of a shear product present after release of pressure.

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