TABLE I. High-spin isomer shifts at 298°K (mm/sec) (relative to metallic iron).

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	170
$Fe(phen)_2X_2$							
Cl	1.00	0.97	0.92	0.89	0.85	0.77	0.74
Br	0.96	0.94	0.91	0.88	0.84	0.77	0.74
NCS	1.01	1.02	0.95	0.88	0.81	0.69	0.67
NCSe	1.02	•••	0.90(62)[b]	0.87	0.82	0.73	0.70
N_3	0.97	0.98	0.92	0.85	0.80	0.69	0.65
NCO	1.00	0.98	0.97	0.94	0.89	0.81	0.79
$CN(1H_2O)$[a]	•••	•••	•••	0.78(90)	0.72	0.60(123)	•••
$\frac{1}{2}C_2O_4(5H_2O)$	•••	1.00	0.99	0.97	0.94	0.92	0.92
$Fe(phen)_3X_2$							
$Cl(7H_2O)$	•••	•••	1.00	0.96	0.92	0.83	0.80
$SCN(1H_2O)$	•••	•••	0.96	0.91	0.86	0.76	0.73
$N_3(6H_2O)$	•••	•••	0.97	0.92	0.87	0.81	0.79
$NCO(nH_2O)$	•••	•••	1.01	0.97	0.93	0.88	0.85
$Fe(bipy)_2X_2$							
$CN(3H_2O)$	•••	•••	1.16(60)	1.14	1.10	0.90	0.78
$\frac{1}{2}C_2O_4(3H_2O)$	•••	•••	1.08	1.01	0.98	0.94	0.93
$Fe(bipy)_3X_2$							
$Cl(5H_2O)$	•••	•••	0.94	0.92	0.90	0.85	0.83
$N_3(5H_2O)$	•••	•••	0.92(63)	0.90	0.87	0.80	0.77

[a] Denotes the known number of molecules of water of hydration. [b] Data point at pressure designated in parentheses.

TABLE II. Low-spin isomer shifts at 298°K (mm/sec) (relative to metallic iron).

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	175
$Fe(phen)_2X_2$							
Cl	•••	0.11	0.38	0.50	0.50	0.47	0.46
Br	•••	0.22	0.42	0.40	0.38	0.35	0.34
NCS	0.35	0.32	0.27	0.24	0.23	0.21	0.20
NCSe	0.32	0.29	0.25	0.23	0.22	0.21	0.21
N_3	0.29	0.34	0.31	0.29	0.27	0.24	0.23
NCO	0.20	0.27	0.31	0.29	0.29	0.28	0.28
$CN(1H_2O)$[a]	0.15	0.13	0.10	0.06	0.02	−0.01(125)[b]	•••
$Fe(phen)_3X_2$							
$Cl(7H_2O)$	0.29	0.27	0.25	0.24	0.24	0.23	0.23
$SCN(1H_2O)$	0.30	0.28	0.25	0.24	0.23	0.21	0.21
$N_3(6H_2O)$	0.29	0.27	0.25	0.24	0.23	0.22	0.22
$NCO(nH_2O)$	0.31	0.28	0.25	0.22	0.20	0.17	0.15
$Fe(bipy)_2X_2$							
$CN(3H_2O)$	0.16	0.13	0.10	0.08	0.06	0.03	0.01
$Fe(bipy)_3X_2$							
$Cl(5H_2O)$	0.28	0.25	0.23	0.22	0.21	0.20	0.20
$N_3(5H_2O)$	0.30	0.26	0.23	0.21	0.20	0.19	0.19

[a] Designated number of waters of hydration in parentheses. [b] Data point at pressure designated in parentheses.

TABLE III. Intermediate-spin isomer shifts at 298°K (mm/sec) (relative to metallic iron).

Compounds	Pressure (kilobars)						
	10	25	50	75	100	150	170
$Fe(phen)_2(C_2O_4)\cdot 5H_2O$	0.35	0.37	0.41	0.45	0.49	0.54	0.54
$Fe(bipy)_2(C_2O_4)\cdot 3H_2O$	0.29	0.28	0.28	0.28	0.30	0.32	0.33

bis- and trisphenanthroline complexes and the interpretation of the transitions between high and low spin states. The last sections discuss an intermediate-spin case, and finally, some bipyridyl–iron complexes.

BISPHENANTHROLINE COMPOUNDS

In the bisphenanthroline compounds the back bonding of the metal $3d$ electrons to the phenanthroline π^* orbitals is probably about the same for all complexes. It is convenient to classify the complexes according to the degree of back bonding to the other two ligands. Complexes with halide ligands, i.e., chlorine or bromine [$Fe(phen)_2Cl_2$ and $Fe(phen)_2Br_2$], have the lowest total amount of back bonding since the chlorine or bromine ions have no empty ligand levels of π symmetry to bond to the ferrous ion. These compounds are high spin. The bisphenanthroline compounds of the form $Fe(phen)_2X_2$ where X equals NCS, NCSe, NCO, and N_3 exhibit a moderate degree of back bonding since in this case back bonding can occur to empty π^* levels in these anionic ligands. The total amount of back donation is still low enough that these compounds are high spin at atmosphereic pressure. $Fe(phen)_2(CN)_2\cdot H_2O$ exhibits a very high degree of back bonding to the empty cyanide ligand π^* levels and exists in a low-spin ground state at 1 atm.

TABLE IV. High-spin quadrupole splittings (mm/sec).[a]

Compound	Pressure (kilobars)						
	10	25	50	75	100	150	170
$Fe(phen)_2X_2$							
Cl	2.99	2.95	2.85	2.79	2.77	2.72	2.71
Br	2.92	2.95	2.81	2.73	2.68	2.60	2.58
NCS	2.61	2.48	2.48	2.51	2.53	2.56	2.58
NCSe	2.50	···	2.55(60)[c]	2.54	2.52	2.47	2.44
N_3	2.73	2.62	2.53	2.52	2.53	2.58	2.60
N_3	2.52	2.41	2.34	2.35	2.39	2.45(120)	··· (383°K)
NCO	2.81	2.77	2.68	2.61	2.56	2.53	2.53
$CN(1H_2O)$[b]	···	···	···	1.61(90)	1.56	1.45(120)	···
$CN(1H_2O)$	···	···	1.76(60)	1.81	1.87	1.88	··· (383°K)
$\frac{1}{2}C_2O_4(5H_2O)$	···	2.51	2.65	2.71	2.74	2.75	2.75
$\frac{1}{2}C_2O_4(5H_2O)$	···	2.36	2.42	2.46	2.48	2.50	2.51 (383°K)
$Fe(phen)_3X_2$							
$Cl(7H_2O)$	···	···	2.62	2.64	2.66	2.69	2.71
$SCN(1H_2O)$	···	···	2.56	2.60	2.63	2.70	2.73
$N_3(6H_2O)$	···	···	2.57	2.57	2.60	2.68	2.72
$NCO(nH_2O)$	···	···	2.66	2.64	2.63	2.60	2.59
$Fe(bipy)_2X_2$							
$CN(3H_2O)$	···	···	2.11(60)	2.10	2.07	1.95	···
$CN(3H_2O)$	···	···	2.03(60)	2.01	1.97	1.90	··· (383°K)
$\frac{1}{2}C_2O_4(3H_2O)$	···	···	2.51	2.57	2.61	2.68	···
$\frac{1}{2}C_2O_4(3H_2O)$	···	···	2.38	2.46	2.50	2.55	··· (383°K)
$Fe(bipy)_3X_2$							
$Cl(5H_2O)$	···	···	2.52(60)	2.60	2.71	2.84	···
$N_3(5H_2O)$	···	···	2.61	2.63	2.65	2.69	···

[a] All values are for 298°K isotherms unless otherwise designated.
[b] Waters of hydration designated in parentheses.
[c] Data point at pressure designated in parentheses.