

FIG. 2. (a) Mössbauer spectra for ACA(1). (b) Mössbauer spectra for ACA(1) (cont'd.).

move strain by powdering the sample, the spectrum returns substantially to the ferric state (see lower part of Fig. 2b). The strain removal process is inefficient with such a small sample; we feel that complete release of strain would probably give an entirely ferric spectrum. In Figs. 3 and 4 are plotted the raw data for the ferrous and ferric isomer shifts for ACA(1) to give some idea of the scatter. Smoothed values for isomer shifts and quadrupole splittings appear in Tables I and II. The classification of compounds is discussed a little later in the paper.

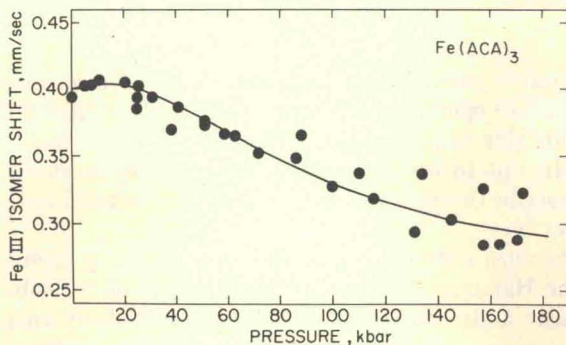


FIG. 3. Fe(III) isomer shift vs pressure—ACA(1).

Isomer Shifts

In analyzing the factors influencing the degree of conversion of Fe(III) to Fe(II) with pressure, it is desirable to have a measure of the tendency of the ligand to donate or withdraw electrons at high pressure. There are a number of possible measures of this tendency at one atmosphere, which, as we shall show, correlate well with the ferric isomer shift.

One measure of the electronic character of the β -diketone is the acid dissociation constant associated with the enol form in the keto-enol equilibrium. Substituent effects are analyzed in terms of the tendency

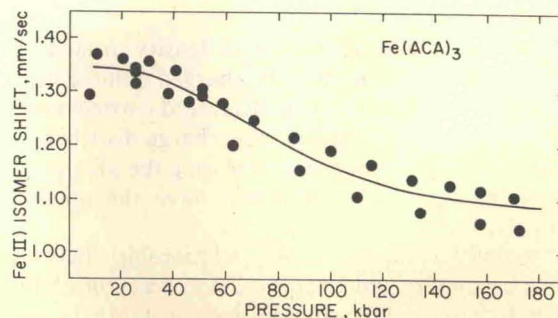


FIG. 4. Fe(II) isomer shift vs pressure—ACA(1).

TABLE I. Isomer shifts vs pressure Fe(III) isomer shift.^a Pressure (kbar).

Derivative	Atm	20	40	60	80	100	120	140	160	180
Class A										
ACA(1)	0.394	0.399	0.385	0.368	0.350	0.335	0.322	0.309	0.299	0.294
BA(4)	0.390	0.389	0.385	0.372	0.347	0.314	0.288	0.267	0.253	0.243
TFACA(5)	0.458	0.420	0.396	0.379	0.362	0.345	0.330	0.316	0.305	0.295
MACA(9)	0.357	0.372	0.374	0.365	0.353	0.343	0.333	0.325	0.316	0.310
NACA(11)	0.429	0.423	0.413	0.402	0.389	0.376	0.366	0.355	0.346	0.336
EACA(12)	0.362	0.358	0.345	0.335	0.328	0.322	0.318	0.315	0.314	0.313
Class B										
FTFA(6)	0.450	0.430	0.419	0.419	0.425	0.437	0.446	0.448	0.449	0.449
TTFA(7)	0.455	0.436	0.424	0.416	0.409	0.404	0.400	0.397	0.394	0.390
BTFA(8)	0.462	0.444	0.427	0.410	0.398	0.390	0.384	0.381	0.380	0.379
PACA(10)	0.370	0.419	0.435	0.437	0.436	0.432	0.428	0.423	0.417	0.413
Class C										
DBM(2)	(0.250)	(0.315)	0.376	0.439	0.481	0.505	0.516	0.521	0.524	0.524
DPM(3)	(0.250)	0.328	0.400	0.441	0.478	0.508	0.529	0.544	0.549	0.550
Fe(II) Isomer shift. Pressure (kbar).										
Derivative	40	60	80	100	120	140	160	180		
Class A										
ACA(1)	1.320	1.267	1.213	1.171	1.141	1.116	1.095	1.081		
BA(4)	1.290	1.215	1.159	1.119	1.088	1.066	1.052	1.042		
TFACA(5)	1.290	1.239	1.199	1.171	1.150	1.132	1.115	1.098		
MACA(9)	1.276	1.269	1.227	1.178	1.141	1.120	1.111	1.106		
NACA(11)	1.260	1.226	1.200	1.177	1.158	1.148	1.143	1.140		
EACA(12)	1.286	1.249	1.213	1.181	1.157	1.141	1.131	1.125		
Class B										
FTFA(6)	1.135	1.084	1.065	1.063	1.063	1.063	1.063	1.063		
TTFA(7)	(1.10)	1.069	1.046	1.027	1.015	1.006	1.001	0.996		
BTFA(8)	1.100	1.074	1.058	1.049	1.044	1.041	1.040	1.039		
PACA(10)	1.066	1.059	1.051	1.046	1.041	1.038	1.034	1.030		
Class C										
DBM(2)	1.095	1.014	0.991	0.989	0.989	0.989	0.989	0.989		
DPM(3)	1.171	1.150	1.128	1.108	1.089	1.074	1.060	1.050		

^a Relative to *bcc* iron, mm/sec.

to increase or reduce the electron density around the oxygen atoms in the negatively charged anionic form. Electron donating groups will increase the oxygen electron density and destabilize the charge distribution, thus lowering the acidity and increasing the pK_D value. Electron withdrawing groups will have the opposite effect.

A second semiquantitative relationship between chemical structure and electron donor-acceptor ability is given by electrophilic substitution constants. In general such correlations have been applied mainly to

aromatic systems where both inductive and resonance effects are operative. However, to the extent that the chelate ring is quasiaromatic in nature, it is reasonable to attempt to use electrophilic substitution constants to describe the electronic properties of the metal chelate derivatives.

The most common method of doing this is by means of the Hammett σ , which is characteristic of the substituent added to the parent structure. Substituents with positive σ values are stronger electron acceptors than hydrogen; negative values indicate a weaker tend-