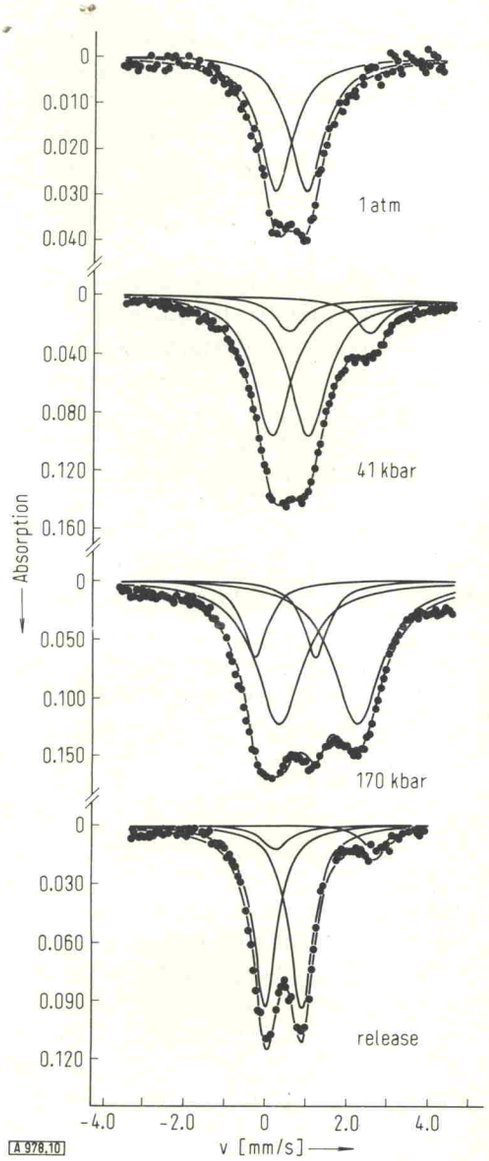


Fig. 10. Mössbauer spectra of tris(2,4-pentanedionato)iron(III) at various pressures.

One would expect that, for a series of related compounds, the conversion would correlate with the electron donor abilities of the ligands. One such study involves the chelates of β-diketones shown in Table 2[9, 33]. At one atmosphere one can measure relative donor character of the ligands by such parameters as the acid dissociation constant, the Hammett σ, the appearance potential from mass spectroscopy, or the half wave potential from polarography. These measurements cannot be obtained on the solid under pressure. However, they correlate well with the ferric isomer shift; a lower isomer shift corresponds to better donor ability. With increasing pressure, the ligand nonbonding orbitals approach the metal 3d orbitals in energy, so the reduction, in general, increases with pressure. This tendency will be augmented in those systems where the isomer shift decreases (relative electron donor ability increases) with pressure, and diminished where the isomer shift increases (relative donor ability decreases). Figure 12 shows the change of conversion between 60 and 160 kbars for the series of compounds of Table 2, plotted against the change of isomer shift in this pressure range. The expected relationship applies very well.

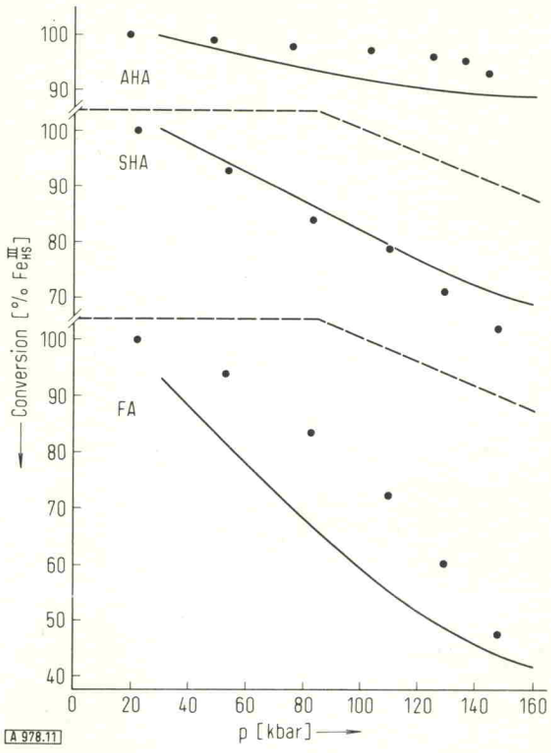
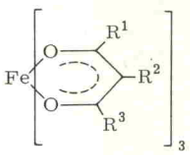


Fig. 11. Comparison of conversion of Fe^{III} to Fe^{II}—from optical (•) and Mössbauer data (—).

Table 2. Tris(β-diketonato)iron(III) complexes.



Ligand	R^1	R^2	R^3
(1)	CH_3	H	CH_3
(2)	C_6H_5	H	C_6H_5
(3)	$C(CH_3)_3$	H	$C(CH_3)_3$
(4)	C_6H_5	H	CH_3
(5)	CF_3	H	CH_3
(6)	CF_3	H	2-Furyl
(7)	CF_3	H	2-Thienyl
(8)	CF_3	H	C_6H_5
(9)	CH_3	CH_3	CH_3
(10)	CH_3	C_6H_5	CH_3
(11)	CH_3	NO_2	CH_3
(12)	CH_3	C_2H_5	CH_3

We can also use Eq. (1) to relate the location and half-width of the charge transfer peak to the reduction of Fe(III). In Table 3 there are shown, for three ferric hydroxamates and the related protein ferrichrome A, the pressure at which 10% reduction occurs, the location and half-width of the charge transfer peak, and the resultant value of E_{th} (assuming $\omega = \omega'$). It can be seen, as one would expect, that within the accuracy of the data and of the analysis $E_{th} \approx 0$.

A recent study[34] on complexes of Cu(II) with organic ligands shows that reduction occurs for these compounds also at high pressure. Cu(II) has nine 3d electrons and Cu(I) has ten. Because of the filled 3d shell, Cu(I) has no d-d excitations. As illustrated in Fig. 13 for $Cu(dtc)_2$ (dtc = diethyldithiocarbamate) the conversion is demonstrated by a decrease in integrated intensity of the Cu(II)-ligand charge transfer peak (b)

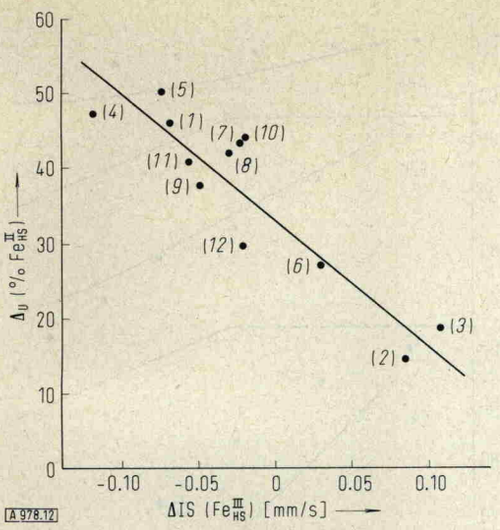


Fig. 12. Change in conversion of Fe^{III} to Fe^{II} *vs* change in isomeric shift between 60—160 kbar.

Table 3. Optical and thermal excitation: Ligand-metal charge transfer in ferric hydroxamates and ferrichrome A (10% reduction of Fe(III).

Ligand	p [kbar]	$h\nu_{max}$ [eV]	$\delta E_{1/2}$ [eV]	E_{th} [eV]
AHA	125	2.80	0.90	0.11
BHA	105	2.70	0.875	−0.06
SHA	70	2.54	0.84	−0.02
FA	37	2.65	0.835	+0.11

and growth of a new peak (c) at lower energy—in a region typical for cuprous charge transfer peaks. Furthermore, the d-d excitation [peak (a)] near 16 kK also decreases in intensity as one would expect.

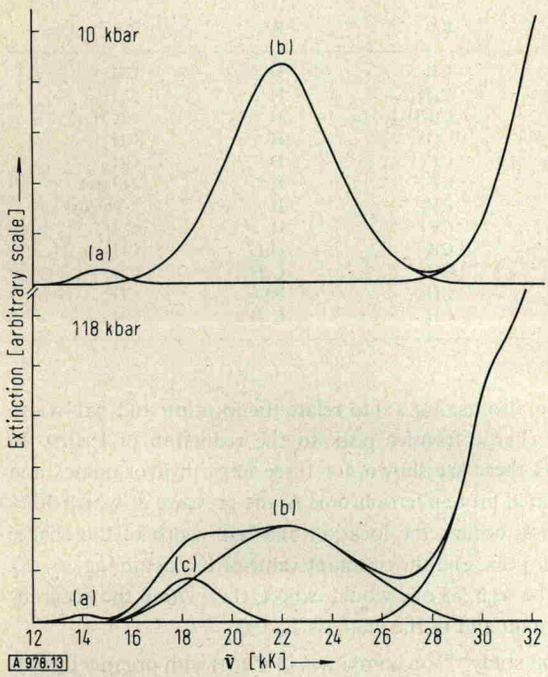


Fig. 13. Optical spectrum of $Cu(dtc)_2$ at various pressures.

The ferric porphyrins have been widely studied as prototypes for hemoglobin, although the applicability is limited by the fact that iron in hemoglobin is apparently in the ferrous state. Porphyrin is a planar molecule with four pyrrole rings connected by methine groups. There are various substituents on the periphery of the pyrroles. In hemin and hematin there is respectively, one Cl^- or one OH^- coordinated axially to the iron which is some 0.5 Å out of the plane of the ring and is high spin. The high spin state would be very improbable with the iron in the plane. In imidazole protoheme two imidazoles are coordinated axially to the iron which is in the plane of the ring and is low spin. Of course, it is something of an oversimplification to speak of definite spin states and oxidation states for iron where the bonding is so complex.

With pressure the ferric ion reduces in all three compounds[9]. At relatively high pressure the ferrous ion produced appears to be in an intermediate spin state in all three cases. For the imidazole protoheme the increase in spin multiplicity is caused by decreased back donation to the imidazoles. For the hemin and hematin the decrease in spin state is apparently associated with the effect of pressure in forcing the iron back into the molecular plane. The large increase in the ferric quadrupole splitting which is observed is consistent with this interpretation.

These reductions illustrate an electronic transition resulting from the shift of energy levels of one member of a complex (the ligand) with respect to those of the other member (the metal).

4. Summary

We have shown that pressure has a very significant effect on the relative energy of electronic orbitals. In a wide variety of circumstances the relative change in energy is sufficient to establish a new, or a greatly modified ground state. These electronic transitions occur in a wide variety of materials; here we have emphasized changes in the coordination chemistry of transition metal ions. It is hoped that this brief outline will amply demonstrate the power of pressure as a tool for investigating electronic structure.

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