

- (17) N. Hofman-Bang and I. Wulff, *Acta Chem. Scand.*, **9**, 1230 (1955).
 (18) J. C. Sullivan and R. C. Thompson, *Inorg. Chem.*, **6**, 1795 (1967).
 (19) K. O. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **13**, 1712 (1974).
 (20) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973).
 (21) W. A. Pryor, "Mechanisms of Sulfur Reactions", McGraw-Hill, New York, N.Y., 1962, pp 59-62.
 (22) R. H. Moore and R. K. Ziegler, Report No. LA-2367, plus Addenda, Los Alamos Scientific Laboratory, Los Alamos, N.M., 1959.
 (23) G. Davies and B. Warnqvist, *Coord. Chem. Rev.*, **5**, 349 (1970).
 (24) G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).
 (25) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).
 (26) G. Davies and K. O. Watkins, *Inorg. Chem.*, **9**, 2735 (1970).
 (27) (a) G. E. Adams, G. S. McNaughton, and B. D. Michael in "The Chemistry of Ionization and Excitation", G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, pp 281-293; (b) G. E. Adams, G. S. McNaughton, and B. D. Michael, *Trans. Faraday Soc.*, **64**, 902 (1968); (c) M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, **77**, 990 (1973).

Contribution from the Materials Science Laboratories, Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712

Empirical Bonding Relationships in Metal-Iron-Sulfide Compounds

J. T. HOGGINS and H. STEINFINK*

Received January 13, 1976

AIC60034P

A bond valence-bond length relationship for bonds between sulfur and iron, where high-spin iron is coordinated by sulfur only, has been derived using the method of Brown and Shannon. This relationship, $V = 1/3 \sum_i (R_i/2.515)^{-6.81}$, is constrained so that the sum of the bond valences around iron is equal to its electrostatic valence, V . The calculated valence is especially useful in structures where direct metal-metal interactions give rise to mobile electrons. The Mössbauer isomer shift, δ , for iron tetrahedrally coordinated by sulfur has been related to the electrostatic valence by the equation $\delta = 1.4 - 0.4V$. The predicted values for isomer shifts and magnetic moments are compared to the measured values for several metal-iron-sulfide and organometallic compounds. This approach interrelates the valence, Mössbauer isomer shift, effective magnetic moment, and electrical conductivity in metal-Fe-S compounds.

Introduction

A series of Ba-Fe-S compounds has been synthesized in our laboratories, and their physical properties have been studied.¹⁻⁵ The properties have been shown to depend on the oxidation states of iron and these need not necessarily correspond to the values expected on the basis of stoichiometry. Robin and Day⁶ have surveyed the mixed-valence chemistry and its influence on the physical properties of a large number of compounds but have excluded sulfides because the ease of electron delocalization in such covalent metal-ligand bonds makes the effects difficult to distinguish from those due to the presence of mixed-valence states. We have developed a relationship between bond valence-bond length and Mössbauer isomer shift that permits the determination of the oxidation state of iron in metal-Fe-S compounds.

A set of empirical bond valence-bond length functions was derived by Brown and Shannon⁷ for several cations in oxides based on the equation

$$V = s_0 \sum_{i=1}^{CN} (R_i/R_0)^{-N}$$

where V is the valence, R_i is the bond distance, and CN is the coordination number. The constants s_0 , R_0 , and N were adjusted so that the equation will predict the valence of an ion at a given site using only the observed bond distances. This is of particular use in structures where the cation is in mixed coordination and/or mixed valence states or the electrons are mobile so that an average oxidation state exists in the crystal.

This approach is used in the metal-iron-sulfur system to determine the oxidation state of the high-spin iron ion. These valences are then used to predict various physical properties which are compared to the values observed in these materials, i.e., Mössbauer isomer shift (δ), magnetic moment (μ), room-temperature electrical resistivity (ρ), and the valence based on stoichiometry. The average Fe-S distance is 2.370 Å in compounds which contain Fe²⁺ in tetrahedral coordination,^{2,8,9} and the average Fe-S distance is 2.233 Å^{10,11} in compounds which contain Fe³⁺ in tetrahedral coordination. These two average distances and oxidation states were used

in the Brown and Shannon formula to determine the arbitrary constants R_0 and N . The constant s_0 was chosen as $1/3$; i.e., the R_0 thus calculated is a hypothetical value for Fe²⁺ in an octahedral environment. The resultant equation for the iron-sulfur compounds is

$$V = 1/3 \sum_i (R_i/2.515)^{-6.81}$$

or

$$V = 178.2 \sum_i R_i^{-6.81} \quad (1)$$

The Mössbauer isomer shift, δ , has been related to the electrostatic valence of iron in many materials. Isomer shift values of 0.60 and 0.20 mm/s are typical values for high-spin Fe²⁺ and Fe³⁺, respectively,⁴ in metal-iron-sulfide compounds when iron is tetrahedrally coordinated by sulfur. Intermediate isomer shift values are interpreted to mean delocalization of electrons and an averaged electrostatic valence. The isomer shift may be written as

$$\delta = A - C|\Psi(0)|^2$$

where $\Psi(0)$ is the electronic wave function at a radius of zero, i.e., in the vicinity of the atomic nucleus of the iron. Only s wave functions are nonzero at the nucleus and thus affect the isomer shift. An increase in s -electron density at the iron nucleus on going from a 3d⁶ to a 3d⁵ configuration arises as a consequence of the decrease in shielding of the 3s and 4s electrons by the removal of the d electron. The change in the valence, ΔV , in going from Fe²⁺ to Fe³⁺ is one d electron which would increase $|\Psi(0)|^2$ and decrease δ . Thus as V increases, $|\Psi(0)|^2$ increases, which can be written as

$$V \approx K|\Psi(0)|^2 + \text{constant}$$

assuming a linear variation of $|\Psi(0)|^2$ with V . Rewriting the equation for the isomer shift yields

$$\delta = A' - C'V$$

The constants A' and C' can be evaluated from typical values

Table I. Results of Bond Valence Correlations

Compd	$V_{\text{calcd.}}$ vu ^g	$V_{\text{obsd.}}$ vu	$\delta_{\text{calcd.}}^a$ mm/s	$\delta_{\text{obsd.}}^a$ mm/s	$\mu_{\text{calcd.}}$ μ_B	$\mu_{\text{obsd.}}$ μ_B	ρ , Ω cm	Fe-Fe, Å	Ref
Ba ₆ Fe ₃ S ₁₅	2.43	2.25	0.43	0.47	5.3	5.6	1.0	2.8	3, 4
Ba ₂ FeS ₃	1.90	2.00	0.64	0.62	4.8	5.3	10 ^d	4.3	3, 4
BaFe ₂ S ₃	2.64	2.00	0.34	0.41	5.5	4.9	0.5	2.7	3, 4
Ba ₇ Fe ₆ S ₁₄ (1) ⁿ	2.59	2.33	0.36	0.36	5.4	5.3	10 ^g	2.8	1, 4
(2)	2.56		0.38	0.36					
(3)	2.32		0.47	0.52					
Ba ₃ FeS ₅	2.91	4.00	0.23	0.17	5.8	5.1	10 ^g	6.3	5
Ba ₁₅ Fe ₇ S ₂₅ (1)	2.76	2.86	0.29	0.22	5.7	5.8	10 ^g	2.7	5
(2)	2.72		0.31						
(3)	2.98		0.21						
(4)	2.84		0.27						
(5)	2.90		0.24						
(6)	2.64		0.34						
(7)	2.80		0.28						
Ba ₅ Fe ₉ S ₁₈ (1)	2.53	2.89	0.39	5.7	5.7	1.0	2.7	20	
(2)	2.99		0.20						
(3)	2.90		0.24						
(4)	2.82		0.27						
(5)	2.68		0.33						
CuFeS ₂	2.79	3.00	0.28	0.22	5.7	3.9	~0.1	~3.5	4, 11, 21
Cu ₂ FeSnS ₄	2.06	2.00	0.58	0.57	5.0				4, 22
CuFe ₂ S ₃	2.77	2.50	0.29	0.39	5.7	<i>d</i>	10	2.8	4, 21, 23
KFeS ₂	3.03	3.00	0.19	0.18	5.9	<i>d</i>	10 ^g	2.7	10, 24, 25
RbFeS ₂	3.22	3.00	0.11	0.19	5.9	<i>d</i>		2.7	10, 24
CsFeS ₂	3.07	3.00	0.17	0.18	5.9	<i>d</i>		2.6	10, 24
NaFeS ₂	<i>e</i>	3.00		0.36		<i>d</i>			10, 24
FeCr ₂ S ₄	2.18	2.00	0.53	0.60	5.1	4.2 ^b	10	~4	26
FeIn ₂ S ₄	1.77	2.00	0.69	0.88				~3.8	4, 27
Fe ₂ SiS ₄ (1)	1.99	2.00	0.60	0.89	5.4	<i>d</i>	1.0	3.6	28, 29
(2)	1.92		0.64						
Fe ₂ GeS ₄ (1)	1.99	2.00	0.60	0.89	5.4	<i>d</i>	1.0	3.6	28, 29
(2)	1.91		0.64						
Fe ₇ S ₈ ^h (1)	2.52	2.29	0.39	0.60	5.4	<i>d</i>	1.0	2.9	30, 31
(2)	2.44 ^c		0.42	0.58					
(3)	2.44		0.42	0.60					
(4)	2.46		0.41	0.62					
Fe ₇ S ₈ ⁱ (1)	2.47	2.00	0.41	5.4	5.4	<i>d</i>	1.0	~3.0	32
(2, 3, 4)	2.68		0.33						
(5, 6, 7)	2.33		0.47						
FeS ^j	2.27	2.00	0.49	0.77	5.2	4.9 ^b		2.9	33-35
FeS ^k	3.03	2.00	0.19	0.35	5.9	4.9 ^b	2	2.6	18
Fe ₃ S ₄ ^l (1)	3.92	3.0	<i>f</i>	0.25	5.0	<i>m</i>	0.1	3.5	36, 37
(2)	2.23	2.5	0.51	0.54	5.1				

Compd	$V_{\text{calcd.}}$ vu	$V_{\text{obsd.}}$ vu	$\delta_{\text{calcd.}}$ mm/s	$\delta_{\text{obsd.}}$ mm/s	$\mu_{\text{calcd.}}$ μ_B	$\mu_{\text{obsd.}}$ μ_B	Fe-Fe, Å	Ref
[(<i>n</i> -Bu) _n N] ₂ [FeS ₂ (CH ₃) ₂] ₂	3.27	3.00	0.09		5.7		3.4	38
(<i>n</i> -Bu) ₄ NFe[S ₂ C ₂ (CN) ₂] ₂	3.46	3.00	0.04	0.23	5.8	<i>d</i>	3.1	39, 40
[Ph ₄ As] ₂ Fe[S ₂ C ₂ (CN) ₂] ₃	4.09	4.00	<i>f</i>		4.9	2.8		41
Fe(S ₂ CN(<i>n</i> -Bu) ₂) ₃	2.62	3.00	0.35		5.5	5.3		42
Fe[S ₂ CN(CH ₃) ₄] ₃	2.71	3.00	0.32		5.6	5.9		43
Fe{[SP(CH ₃) ₂] ₂ N} ₃	2.06	2.00	0.58	0.67	5.0	5.3		4, 44
[Ph ₄ As] ₂ Fe ₄ S ₄ [S ₂ C ₂ (CF ₃) ₂] ₄ (1)	4.00	3.50	<i>f</i>	0.14	4.9	1.0	2.6	45
(2)	3.79							
(3)	4.61							
(4)	3.80							
(Et ₄ N) ₂ Fe ₄ S ₄ (SCH ₂ Ph) ₄ (1)	2.61	2.64	0.36	>2.50	5.5	1.0	2.7	46
(2)	2.64		0.34					
(3)	2.67		0.33					
(4)	2.63		0.35					

^a Isomer shifts are relative to α -Fe. ^b From neutron diffraction. ^c Error in reported distances. ^d Antiferromagnetic. ^e No crystal structure. ^f Equation for isomer shift does not hold for calculated valences above 3+. ^g Valence units. ^h Monoclinic; pyrrhotite. ⁱ Trigonal; pyrrhotite. ^j Troilite. ^k Mackinawite. ^l Greigite. ^m Ferrimagnetic. ⁿ Fe site number.

of δ mentioned above. The result is

$$\delta = 1.4 - 0.4V \quad (2)$$

in units of mm/s with respect to metallic iron.

This last equation can only be used to correlate isomer shift of high-spin iron when tetrahedrally coordinated by sulfur. When the coordination is octahedral, the isomer shift should be larger than that estimated by the above equation. This variation of isomer shift with coordination number has been observed in other compounds.¹² None of the above equations

holds for low-spin iron where iron-sulfur distances are approximately 0.1 Å shorter.¹³ The isomer shift for low-spin iron is approximately 0.30 mm/s and changes very little with oxidation state.¹⁴ Low-spin iron in tetrahedral coordination has not been observed; therefore, the above equations can be used with confidence.

Discussion

A literature survey was made of inorganic and organometallic compounds in which iron is in the high-spin state and

coordinated by sulfur only. The results are summarized in Table I, and the calculated values are compared with the experimentally determined values. The calculated valences were obtained from eq 1, and the observed values are based on the stoichiometry; the calculated isomer shift is obtained from eq 2. Interatomic Fe-Fe distances in the respective compounds are listed in column 9.

Generally the agreement between observed and calculated values and correlation with physical properties are good. Whenever the Fe-Fe distances are 3 Å or less, direct interactions are possible and the isomer shift has a value between 0.6 and 0.2 mm/s. A low value of the resistivity is also observed. This is especially noteworthy in BaFe₂S₃ where on the basis of stoichiometry divalent iron is expected. On the other hand Ba₂FeS₃ has a high resistivity as expected from the isomer shift value and the Fe-Fe distance. However, this type of correlation is not the only result to emerge from this approach. In Ba₇Fe₆S₁₄ the FeS₄ tetrahedra form an infinite zigzag chain in which a trinuclear unit formed by a central tetrahedron sharing opposite edges articulates by corner sharing with the next unit. The isomer shifts indicate that within the trinuclear unit the electrons are delocalized and a resonating structure exists with a lifetime less than 10⁻⁷ s. However, the resistivity is high because the Fe-Fe distances across the corner-shared tetrahedra are 3.7 Å.

A similar trinuclear unit is present in Ba₁₅Fe₇S₂₅ except the central tetrahedron shares one edge and one corner, and, most importantly, they are isolated. The isomer shifts are again intermediate in value so that the electrons are mobile within the edge-sharing unit; the electrical resistivity is high because the short Fe-Fe distances are not continuous.

The delocalization of an electron within a FeS₄⁴⁻ tetrahedron is observed in Ba₃FeS₅. The stoichiometric valence is 4+, but the calculated value is 3+. The observed and calculated isomer shifts indicate the presence of Fe³⁺. The presence of tetravalent iron in a sulfide is not very likely, and indeed it appears that an electron is effectively back-donated to the iron ion, thus reducing its charge. In other words, upon going from Fe²⁺ to Fe³⁺, i.e., from FeS₄⁶⁻ to FeS₄⁵⁻, the electron will be removed from a mainly Fe orbital;¹⁵ hence a change in isomer shift will be observed. However with further oxidation to FeS₄⁴⁻ the electron will come from an orbital having about 80% sulfur character.¹⁶ This electron would have little effect on the iron nucleus so a typically Fe³⁺ Mössbauer isomer shift is observed.

The structures of KFeS₂, RbFeS₂, and CsFeS₂ display infinite chains of edge-sharing FeS₄ tetrahedra, although they are not isostructural. It is noteworthy that even though the Fe-Fe distances are 2.7 Å, the isomer shift indicates that the electrons are localized and the calculated valence sum is 3+. The resistivity is relatively high. These compounds probably illustrate the remark by Robin and Day⁶ that in sulfides a relatively small expenditure of energy is required to delocalize an electron and this is probably the cause of the intermediate resistivity value; it is not due to the presence of a mixed oxidation state. No structural information is available for NaFeS₂, but the reported isomer shift indicates an electronic delocalization. A knowledge of the Fe-Fe distances is essential in order to predict the electrical properties.

An apparent anomaly exists in the data correlation for CuFeS₂, chalcopyrite. The structure is a superlattice of zinc blende. The authors¹¹ found longer than normal Fe-S distances and attributed this to a resonating Fe³⁺Cu⁺ ⇌ Fe²⁺Cu²⁺ structure. We suggest, on the basis of the observed isomer shift, that this resonance does not occur, but instead a static disorder exists in which about 5-10% of the tetrahedral sites are randomly occupied by Fe³⁺ and Cu⁺. We predict that this should be a high-resistivity material at room tem-

perature. The electrical conductivity data show that the observed behavior to a temperature of about 300 °C reflects the contribution of impurities to conduction.¹⁷ The extrapolation of the intrinsic portion of the conductivity curve to room temperature indicates that CuFeS₂ would have a resistivity of about 10⁴-10⁵ Ω cm. In cubanite, CuFe₂S₃ electron delocalization is present, and the data fit the theory.

The correlations which we have discussed are based on the tetrahedral coordination of iron. Its presence in an octahedral environment should severely modify or, even, negate these correlations. In the normal spinel FeCr₂S₄ the data show that Fe²⁺ is, indeed, in the tetrahedral position, and its electrons are localized. The low resistivity must be due to the interactions among the octahedral chromium ions. FeIn₂S₄ is an inverse spinel with iron and indium in the octahedral sites; therefore, calculated and observed valences do not agree. Since the isomer shift is larger for octahedral than for tetrahedral coordination,¹² the observed value of 0.88 mm/s confirms the structural result that this is an inverse spinel. Approximately the same value of the isomer shift is also observed for octahedral Fe²⁺ in Fe₂GeS₄. It appears that a shift of about 0.9 mm/s is diagnostic for Fe²⁺ in octahedral coordination with sulfur. This value of the isomer shift should be observed in Fe₂SiS₄.

There have been at least five compounds identified with the formula Fe_{1-x}S (0 ≤ x ≤ 0.15) which are stable at room temperature. Most are distortions from the ideal NiAs structure so that iron atoms are octahedrally coordinated by the sulfur atoms, and the Fe-Fe distances are about 3.0 Å or less. As expected, calculated and experimental values show no agreement. Mackinawite which has an anti-PbO structure is the exception to the octahedral coordination, and iron in this compound is tetrahedral. The calculated valence is approximately 3.0 compared to 2.0 based on the formula FeS. The Mössbauer spectrum shows no magnetic ordering down to 1.7 K^{18,19} which is surprising since the Fe-Fe separation is 2.6 Å. No magnetic susceptibility measurements are reported due to the presence of impurities. Bertaut et al. reported an isomer shift at 4.2 K of about 0.49 mm/s. This is approximately 0.3 mm/s larger than that reported at the same temperature by Vaughan et al. The latter paper did not report an isomer shift at room temperature. The electrical resistance in this compound indicates semiconductor behavior, and neutron diffraction results showed a spin of 2.¹⁸ The reported small, unresolved, quadrupole splitting is characteristic of the symmetric d⁵ electronic configuration. These results seem to indicate that the oxidation state of the compound is slightly less than 3.0, which is much larger than indicated by the stoichiometry. The reported isomer shift data differ significantly so no definite conclusion can be based on them, but they seem to indicate trivalent character. This case appears to be similar to the compound BaFe₂S₃.

To test eq 1 and 2, the available data for organometallic compounds were examined and are listed with the calculated values in Table I. The iron coordination polyhedra vary from four to six near neighbors and can be described by tetrahedra, distorted trigonal bipyramids, and distorted octahedra. Nevertheless, fair agreement exists among the calculated and stoichiometric valences and for the Mössbauer isomer shift in the tetrahedral cases.

Conclusion

A strong correlation between bond length and bond valence is observed in iron-sulfur compounds. We also show a correlation between the Mössbauer isomer shift, electrostatic valence, and bond distances. Using these concepts eq 1 and 2 were derived to interrelate the physical and crystal chemical properties of a large number of iron sulfides in which high-spin iron is present. The Mössbauer calculations hold only for

tetrahedrally coordinated Fe. The Mössbauer shift for octahedral Fe²⁺ appears to be 0.90 mm/s. Knowledge of isomer shifts for the compounds Fe[S₂CN(*n*-Bu)₂]₃ and Fe[S₂CN(CH₂)₄]₃, in which iron atoms are in the trivalent oxidation state, would be extremely valuable in order to establish its variation with valence in octahedrally coordinated iron compounds.

Acknowledgment. Financial support for this research effort by the National Science Foundation and the Robert A. Welch Foundation, Houston, Tex., is gratefully acknowledged. The comments of Dr. R. D. Shannon have been very helpful in the preparation of this manuscript, and we wish to thank him also for communicating to us his results on Fe₂SiS₄ and Fe₂GeS₄ prior to their publication.

Registry No. Ba₆Fe₈S₁₅, 37204-48-1; Ba₂FeS₃, 37204-45-8; BaFe₂S₃, 37204-43-6; Ba₇Fe₆S₁₄, 12537-50-7; Ba₃FeS₅, 58915-68-7; Ba₁₅Fe₇S₂₅, 58915-69-8; Ba₅Fe₉S₁₈, 53810-48-3; CuFeS₂, 1308-56-1; Cu₂FeSnS₄, 12019-29-3; CuFe₂S₃, 12140-08-8; KFeS₂, 12022-42-3; RbFeS₂, 12140-50-0; CsFeS₂, 12158-53-1; NaFeS₂, 12160-05-3; FeCr₂S₄, 12018-12-1; FeIn₂S₄, 12292-75-0; Fe₂SiS₄, 59123-33-0; Fe₂GeS₄, 12332-32-0; Fe₇S₈, 12063-67-1; FeS, 1317-37-9; Fe₃S₄, 12063-38-6; [(*n*-Bu)₄N]₂[FeS₂(CH₂)₂]₂, 36841-25-5; (*n*-Bu)₄NFe[S₂C₂(CN)₂]₂, 31358-28-8; [Ph₄As]₂Fe[S₂C₂(CN)₂]₃, 25595-40-8; Fe[S₂CN(*n*-Bu)₂]₃, 14526-32-0; Fe[S₂CN(CH₂)₄]₃, 21288-86-8; Fe[SP(CH₃)₂]₂N₂, 29950-57-0; [Ph₄As]₂Fe₄S₄[S₂C₂(CF₃)₂]₄, 12572-53-1; (Et₄N)₂[Fe₄S₄(SCH₂Ph)₄], 50923-41-6.

References and Notes

- I. E. Grey, H. Hong, and H. Steinfink, *Inorg. Chem.*, **10**, 340 (1971).
- H. Hong, I. E. Grey, and H. Steinfink, *Natl. Bur. Stand. (U.S.), Spec. Publ.*, No. 364 (1972).
- H. Hong and H. Steinfink, *J. Solid State Chem.*, **5**, 93 (1972).
- W. M. Reiff, I. E. Grey, A. Fan, Z. Eliezer, and H. Steinfink, *J. Solid State Chem.*, **13**, 32 (1975).
- J. T. Lemley, J. M. Jenks, J. T. Hoggins, Z. Eliezer, and H. Steinfink, *J. Solid State Chem.*, **16**, 117 (1976).
- M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
- I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, **29**, 266 (1973).
- R. W. G. Wyckoff, "Crystal Structures", Wiley-Interscience, New York, N. Y., 1963.
- A. Davidson and E. S. Switkes, *Inorg. Chem.*, **10**, 837 (1971).
- V. W. Bronger, *Z. Anorg. Allg. Chem.*, **359**, 225 (1968).
- S. R. Hall and J. M. Stewart, *Acta Crystallogr., Sect. B*, **29**, 579 (1973).
- N. E. Erickson, *Adv. Chem. Ser.*, No. **68**, 86 (1967).
- P. C. Healy and A. H. White, *Chem. Commun.*, 1446 (1971).
- J. Danon, "Chemical Applications of Mossbauer Spectroscopy", V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1963, Chapter 3.
- J. G. Norman, Jr., and S. C. Jackels, *J. Am. Chem. Soc.*, **97**, 3833 (1975).
- J. G. Norman, Jr., private communication.
- T. Teranishi, *J. Phys. Soc. Jpn.*, **16**, 1881 (1961).
- E. F. Bertaut, P. Burllet, and J. Chappert, *Solid State Commun.*, **3**, 335 (1965).
- D. J. Vaughan and M. S. Ridout, *J. Inorg. Nucl. Chem.*, **33**, 741 (1971).
- I. E. Grey, *Acta Crystallogr., Sect. B*, **31**, 45 (1975).
- S. Takeno, K. Masumoto, and T. Kamigaichi, *J. Sci. Hiroshima Univ., Ser. C*, **5**, 341 (1968).
- L. O. Brockway, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **89**, 434 (1934).
- M. E. Fleet, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **132**, 276 (1970).
- D. Raj and S. P. Puri, *J. Chem. Phys.*, **50**, 3184 (1969).
- D. O. Cowan, G. Pasternak, and F. Kaufman, *Proc. Natl. Acad. Sci. U.S.A.*, **66**, 843 (1970).
- M. R. Spender and A. H. Morrish, *Can. J. Phys.*, **50**, 1125 (1972).
- H. Hahn and W. Klinger, *Z. Anorg. Allg. Chem.*, **263**, 177 (1950).
- H. Vincent, E. F. Bertaut, W. H. Baur, and R. D. Shannon, to be submitted for publication.
- R. D. Shannon, private communication.
- M. Tokonami, K. Nishiguchi, and N. Morimoto, *Am. Mineral.*, **57**, 1066 (1972).
- D. J. Vaughan and M. S. Ridout, *Solid State Commun.*, **8**, 2165 (1970).
- M. E. Fleet, *Acta Crystallogr., Sect. B*, **27**, 1864 (1971).
- H. T. Evans, Jr., *Science*, **167**, 621 (1970).
- A. F. Andresen, *Acta Chem. Scand.*, **14**, 919 (1960).
- S. Hafner and M. Kalvius, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **123**, 443 (1966).
- B. J. Skinner, R. C. Erd, and F. S. Grimaldi, *Am. Mineral.*, **49**, 543 (1964).
- J. M. D. Coey, M. R. Spender, and A. H. Morrish, *Solid State Commun.*, **8**, 1605 (1970).
- M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973).
- W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).
- N. N. Greenwood and H. J. Whitfield, *J. Chem. Soc. A*, 1697 (1968).
- A. Sequeira and I. Bernal, *J. Cryst. Mol. Struct.*, **3**, 157 (1973).
- B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968).
- P. C. Healy and A. H. White, *J. Chem. Soc. A*, 1163 (1972).
- M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 1778 (1971).
- I. Bernal, B. R. Davis, M. L. Good, and S. Chandra, *J. Coord. Chem.*, **2**, 61 (1972).
- T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiker, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2437 (1972).

Contribution from the Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Molecular Stereochemistry of Two Intermediate-Spin Complexes.

Iron(II) Phthalocyanine and Manganese(II) Phthalocyanine

JOHN F. KIRNER, W. DOW, and W. ROBERT SCHEIDT*

Received January 15, 1976

AIC600426

The molecular stereochemistry of iron(II) phthalocyanine and manganese(II) phthalocyanine has been determined by x-ray diffraction methods. The phthalocyanine ligand constrains the metal ion to effectively square-planar coordination and to an intermediate spin state. The Fe^{II}-N bond distance of 1.926 (1) Å and the Mn^{II}-N bond length of 1.938 (3) Å are wholly consistent with the assignment of an intermediate-spin ground state. Both complexes crystallize as the β polymorph. Crystal data are as follows: for FePc, space group P2₁/a, a = 19.392 (5) Å, b = 4.786 (2) Å, c = 14.604 (4) Å, β = 120.85 (1)°, ρ_{exptl} = 1.61 g/cm³, ρ_{calcd} = 1.623 g/cm³ for Z = 2, required molecular symmetry $\bar{1}$; for MnPc, space group P2₁/a, a = 19.400 (4) Å, b = 4.761 (2) Å, c = 14.613 (3) Å, β = 120.74 (1)°, ρ_{exptl} = 1.61 g/cm³, ρ_{calcd} = 1.625 g/cm³ for Z = 2, required molecular symmetry $\bar{1}$. Intensity data were measured by θ-2θ scanning on a Syntex P1 automated diffractometer using graphite-monochromated Mo Kα radiation. For FePc, the intensities of 3949 reflections with (sin θ)/λ ≤ 0.817 Å⁻¹ were used in the refinement of the 187 structural parameters and for MnPc the intensities of 2158 reflections having (sin θ)/λ < 0.69 Å⁻¹ were employed. Final discrepancy indices are as follows: FePc, R₁ = 0.045, R₂ = 0.057; MnPc, R₁ = 0.066, R₂ = 0.066.

Iron(II) and manganese(II) phthalocyanine have been recognized as examples of a rare type of coordination compound in which the metal ion has an intermediate-spin ground state (Fe, S = 1; Mn, S = 3/2).¹ The basic stereochemistry

of four-coordinate phthalocyanines has been known for some time,^{2,3} but surprisingly the quantitative stereochemistry of the much studied iron(II) and manganese(II) derivatives has not been determined. We report herein the structures of