

AD-A048 223

VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY
PHYSICAL AND CHEMICAL PROPERTIES OF SQUARATE COMPLEXES. I. SPEC--ETC(U)
DEC 77 J. T. WROBLESKI, D B BROWN

F/6 7/2

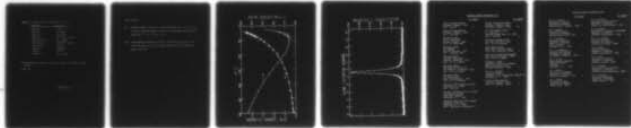
N00014-75-C-0756

UNCLASSIFIED

TR-7

NL

| OF |
AD
A048 223



END
DATE
FILMED
1 -78
DDC

FG

12

AD A 0 4 8 2 2 3

OFFICE OF NAVAL RESEARCH

Contract ¹⁵ N00014-75-C-0756

Project .NR 356-593

⁹ TECHNICAL REPORT, NO. 7

¹⁴ TR-7

⁶ Physical and Chemical Properties of Squarate Complexes. I. Spectral, Magnetic, and Thermal Behavior of Dimeric Iron(III) Squarate,

by

¹⁰ James T. Wroblewski and David B. Brown*

Prepared for Publication

in the

Inorganic Chemistry

University of Vermont

Department of Chemistry

Burlington, Vermont 05401

¹¹ December 8, 1977

¹² 16p.

DDC
RECEIVED
DEC 28 1977
E

Reproduction in whole or in part is permitted for any purpose of the United States Government

Approved for Public Release: Distribution Unlimited.

AD No. _____
DDC FILE COPY

142
408 892

1B

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 7	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "PHYSICAL AND CHEMICAL PROPERTIES OF SQUARATE COMPLEXES. I. SPECTRAL, MAGNETIC, AND THERMAL BEHAVIOR OF DIMERIC IRON(III) SQUARATE"		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) D. B. Brown, J. T. Wroblecki		8. CONTRACT OR GRANT NUMBER(s) ✓ N00014-75-C-0756
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Vermont Burlington, Vermont 05401		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE December 8, 1977
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 12
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted for publication in Inorganic Chemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Squaric acid, iron complexes, magnetic susceptibility, Mössbauer spectroscopy, thermal analysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The magnetic susceptibility behavior of an iron(III) squarate complex with empirical formula $\text{Fe}(\text{C}_4\text{O}_4)(\text{OH})(\text{H}_2\text{O})_3$ has been studied in the range 20-300K. These susceptibilities were best fit to a $S_1=S_2=5/2$ dimer model with $J=6.9 \text{ cm}^{-1}$ and $g=2.00$. Presence of both terminally-coordinated bidentate squarate dianion and bridging hydroxy groups is supported by the infrared spectrum of the dimer. The ^{57}Fe Mössbauer spectrum of this compound consists of a single absorption with $\delta=0.40 \text{ mm/s}$ relative to iron metal. Based on these		

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

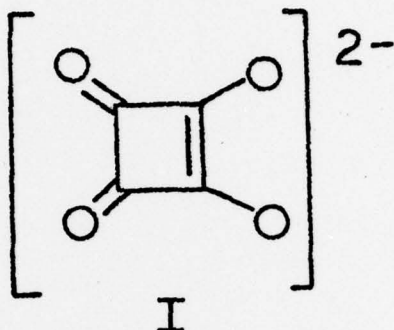
Physical and Chemical Properties of Squarate Complexes. I. Spectral,
Magnetic, and Thermal Behavior of Dimeric Iron(III) Squarate

by

James T. Wroblewski and David B. Brown*

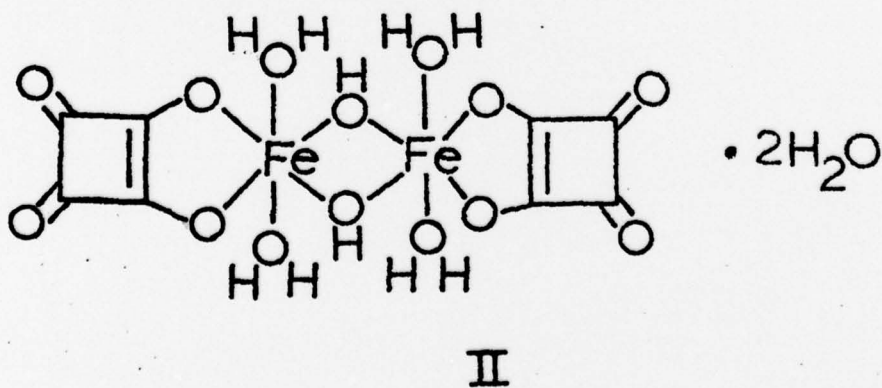
Contribution from the Department of Chemistry
University of Vermont, Burlington, Vermont 05401

Trivalent metal-ion complexes which contain the squarate dianion (I, Sq) with general formula $M(\text{Sq})(\text{OH})(\text{H}_2\text{O})_3$ were first reported by West and Niu¹ (M=Al, Cr, or Fe) and Condren and McDonald² (M=V). Niu's suggestion of a dimeric structure for



$\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_3$ was principally supported by the reduced room temperature magnetic moment of this compound. The other trivalent metal complexes were subsequently assigned dimeric structures based on their x-ray isomorphism to the iron compound.^{1,2}

As part of our investigation of the electronic and structural properties of iron-squarate complexes we have studied the variable-temperature magnetic susceptibility, spectral, and thermal behavior of $\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_3$, and report here evidence which supports a dihydroxy-bridged dimeric structure (II) for this complex.



Experimental Section

Materials and Methods. Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) was purchased from Aldrich Chemical Co. and used as received. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was purified by centrifuging a concentrated ethanolic solution of commercial hydrated ferric chloride and discarding the insoluble material. Magnetic susceptibilities were determined using a conventional Faraday balance calibrated with $\text{Hg}[\text{Co}(\text{NCS})_4]$.⁴ Ligand diamagnetism was treated as usual by assuming $\chi_{\text{sq}} = 30.6 \times 10^{-6}$ cgsu¹ and by using a table at Pascal's constants.⁵ Mössbauer spectra were obtained by using the spectrometer previously described⁶ with a $^{57}\text{Co}(\text{Pt})$ source maintained at room temperature. A moderately-thin foil of natural $\alpha\text{-Fe}$ was used to define the velocity scale. Mössbauer spectra were deconvoluted by assuming pure Lorentzian line shapes superimposed on a parabolic base line. Parameters obtained in this manner were reproducible to $\pm 1\%$. Infrared spectra were obtained on a Beckman IR 20A instrument by using KBr pressed pellets. X-ray powder diffraction patterns were obtained with the Straumanis technique by using vanadium-filtered Cr radiation ($\lambda_{\text{mean}} = 2.2909\text{\AA}$). TGA curves were obtained by using a Dupont 900 Thermal Analyzer coupled to a Dupont 950 Thermogravimetric Analyzer. Iron was determined by EDTA titrimetry. C and H analyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Preparation of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$. $\text{Di}[\mu\text{-hydroxodiaquosquaratoiron(III)}]$ dihydrate was prepared by adding an ethanolic solution of FeCl_3 to a stoichiometric amount of squaric acid dissolved in hot water. The resulting purple solution was refluxed and filtered. Upon cooling a purple-brown material crystallized. This solid was collected, repeatedly washed with cold ethanol, and air dried at room temperature. Anal. Calcd for $\text{FeC}_4\text{H}_7\text{O}_8$: Fe, 23.38; C, 20.11; H, 2.95. Found: Fe, 23.6; C, 19.93; H, 2.84. A partially deuterated analog was prepared by using 90% D_2O as reaction solvent. X-ray powder patterns of the normal and deuterated materials were identical.

Results and Discussion

X-ray powder pattern d-spacings obtained for the samples of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ prepared in this study are identical to those reported by West and Niu¹. Magnetic susceptibility data for $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ given in Table I⁷ and shown in Figure 1 indicate moderate intramolecular antiferromagnetic spin exchange in this material. Both the magnitude and temperature dependence of the susceptibility typify the behavior of an $S_1 = S_2 = 5/2$ dimer.⁸ For such a system the following expression for the susceptibility is obtained from the dipolar coupling approach of Van Vleck.⁹

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \left[\frac{55 + 30 \exp(-10J/kT) + 14 \exp(-18J/kT) + 5 \exp(-24J/kT) + \exp(-28J/kT)}{11 + 9 \exp(-10J/kT) + 7 \exp(-18J/kT) + 5 \exp(-24J/kT) + 3 \exp(-28J/kT) + \exp(-30J/kT)} \right]$$

Symbols in this expression have their usual meanings. A least squares fit of the experimental susceptibility to this equation yields values of J and g. By assuming $g = 2.00$, the smooth curves shown in Figure 1 are obtained for $J = -6.9 \text{ cm}^{-1}$. This value of $|J|$ is inconsistent with both oxo- and squarato-bridged structures. Oxo-bridged Fe(III) dimers are invariably characterized by coupling constants near -100 cm^{-1} .¹⁰ Squarate bridges, on the other hand, provide a poor exchange path as experimentally observed for the polymers $\text{Ni}(\text{Sq})(\text{H}_2\text{O})_2$ ($J = -0.7 \text{ cm}^{-1}$)¹¹ and $\text{Fe}(\text{Sq})(\text{H}_2\text{O})_2$ ($J = -0.7 \text{ cm}^{-1}$)¹² and the dimers $[\text{Cu}_2(\text{Et}_5\text{dien})_2(\text{Sq})](\text{BPh}_4)_2$ ($J = -2.1 \text{ cm}^{-1}$)¹³ and $[\text{Ni}_2(\text{macro})_2(\text{Sq})](\text{ClO}_4)_2$ ($J = -0.4 \text{ cm}^{-1}$).¹⁴ Coupling constants in the vicinity of -10 cm^{-1} have been observed for several dibridged Fe(III) dimers, including dihydroxo-bridged dimers.^{15,16}

A room temperature Mössbauer spectrum of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$, shown in Figure 2, may be described by a single Lorentzian line with isomer shift $\delta = 0.40 \text{ mm/s}$.

If the data are fit to a quadrupole doublet, a splitting of $\Delta = 0.16$ mm/s is obtained with $\delta = -0.40$ mm/s, $\Gamma_1 = 0.40$, and $\Gamma_2 = 0.38$ mm/s. The fit is essentially identical for these two sets of parameters. Although the isomer shift increases to 0.48 mm/s at 19K we do not observe any greater resolution of the quadrupole doublet at low temperature.

Small values of Δ , taken by themselves, do not distinguish tetrahedral from octahedral coordination for Fe(III) nor do they differentiate low-spin Fe(II) from high-spin Fe(III).¹⁷ In general the same applies for δ . Spin state is fortunately easy to diagnose from susceptibility data, but it is more difficult to distinguish T_d from O_h coordination for Fe(III). It has been our general experience that in the absence of magnetically-perturbed Mössbauer data (which may be equivocal for small Δ), it is possible to make this distinction by considering the relative percent effect (percent transmission) of T_d Fe(III) complexes to O_h Fe(III) complexes. Whereas many $[\text{FeX}_4]^-$ complexes show 1-2% effect at room temperature, octahedral Fe(III) compounds at the same temperature realize 10-20% effect. This argument is by no means unequivocal but may be used as a qualitative guide in many instances. The relatively high percent effect shown by $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ at RT (Figure 2) would seem to support octahedral rather than tetrahedral Fe(III) in this compound.

Infrared spectra of squarate-containing compounds are quite characteristic of the mode of coordination.² Thus it is possible to distinguish the terminal form of squarate as in II from the bridging form by virtue of the lower symmetry of the former. Polymeric divalent metal squarates, which contain the squarate ion in approximately D_{4h} symmetry, have as the most prominent feature in their infrared spectra a broad band near 1500 cm^{-1} assigned to a mixture of C-O and C-C stretching modes.^{1,2,12} The infrared spectrum of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ however shows not only this absorption but also moderate bands at 1640 and 1815 cm^{-1} . The former absorption may be assigned

to a C=C stretching mode and the latter to a C=O stretching mode. The infrared spectrum of this complex thus suggests nominal C_{2v} symmetry for the squarate ion, as in squaric acid and metal squarates involving bidentate coordination of the squarate ion. A number of other infrared absorptions are present in the spectrum of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$, all of which are consistent with structure II.¹⁸ These bonds and appropriate assignments are listed in Table II. We have assigned a weak absorption at 850 cm^{-1} to the Fe-O-H deformation mode associated with bridging hydroxo groups.¹⁵ This assignment is supported by the observation that this band decreases in intensity upon partial deuteration.

The thermal weight loss curve of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ obtained in a nitrogen atmosphere shows two inflections. The first, at 160°C , corresponds to a 17.3% weight loss and the second, at 290°C , corresponds to a 64.8% total weight loss. If the first step corresponds only to dehydration then 4.6 moles of water are lost per mole of dimer. An x-ray powder pattern of the final residue shows the presence of iron metal. The total theoretical weight loss is 66.6% if iron metal is the only product of the decomposition. The thermal behavior of this material contrasts markedly with that of the vanadium analog.² The vanadium complex loses two moles of water per dimer at 80° in vacuum, and six moles of water in either air or argon at ca 150° , and, ultimately, decomposes to vanadium oxides, rather than the metal, at higher temperatures. The complexity of the final decomposition step in these complexes has been previously noted both for divalent^{19,20} and trivalent² metal squarates.

Acknowledgement. The authors acknowledge support of this work by the Office of Naval Research.

Supplementary Material Available: A listing of observed magnetic susceptibilities Table I (1 page). Ordering information is given on any current masthead page.

References and Notes

- (1) R. West and H. Y. Niu, J. Am. Chem. Soc., 95, 2589 (1963).
- (2) S. M. Condren and H. O. McDonald, Inorg. Chem., 12, 57 (1973).
- (3) H. Y. Niu, "New Aromatic Anions and Their Complexes", Ph.D. Dissertation, Univ. of Wisconsin, 1962.
- (4) D. B. Brown, V. H. Crawford, J. W. Hall, and W. E. Hatfield, J. Phys. Chem., 81, 1303 (1977).
- (5) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Complexes", Chapman and Hall, London, 1973, p 5.
- (6) C. W. Allen and D. B. Brown, Inorg. Chem., 13, 2020 (1974).
- (7) Supplementary material.
- (8) S. A. Cotton, Coord. Chem. Rev., 8, 185 (1972).
- (9) J. H. Van Vleck, "Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932.
- (10) K. S. Murray, Coord. Chem. Rev., 1 (1974).
- (11) M. Habenschuss and B. C. Gerstein, J. Chem. Phys., 61, 852 (1974).
- (12) J. T. Wroblewski and D. B. Brown, in preparation.
- (13) Et₅dien is 1,1,4,7,7-pentaethyldiethylenetriamine. T. R. Felthouse, E. J. Laskowski, and D. N. Hendrickson, Inorg. Chem., 16, 1077 (1977).
- (14) Macro is 2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane. D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, Inorg. Chem., 12, 985 (1973).
- (15) J. A. Thich, C. C. Ou, D. Powers, B. Vasiliow, D. Mastropaolo, J. A. Potenza, and H. J. Schugar, J. Am. Chem. Soc., 98, 1425 (1976).
- (16) J. T. Wroblewski and G. J. Long, Inorg. Chem., 16, 0000 (1977).
- (17) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London, 1971, p 90 ff.

- (18) A number of workers have discussed the infrared spectra of squaric acid, its anions, and their complexes. See for example: D. P. C. Thackeray and R. Shirley, J. Cryst. Mol. Struct., 2, 159 (1972); D. P. C. Thackeray and B. C. Stace, Spectrochim. Acta, 30A, 1961 (1974); M. Ito and R. West, J. Am. Chem. Soc., 85, 2580 (1963); and G. Doyle and R. S. Tobias, Inorg. Chem., 7, 2484 (1968).
- (19) R. A. Bailey, W. N. Mills, and W. J. Tangredi, J. Inorg. Nucl. Chem. 33, 2387 (1971).
- (20) C. C. Lewchalermwong, "A Study of the Thermal Dehydration and Decomposition of Oxocarbon Anion Salts of Transition Metals", M. S. Thesis, University of North Carolina at Greensboro, 1977.

Table I. Magnetic Susceptibilities and Moments ^a

T, K	χ_M' , cgsu	$\mu_{\text{eff}}/\text{Fe}, \mu_B$	μ_{calc}, μ_B
21.8	0.04054	1.88	1.92
22.1	0.04172	1.92	1.94
23.2	0.04141	1.96	2.00
24.2	0.04216	2.02	2.05
26.3	0.04395	2.15	2.15
27.8	0.04433	2.22	2.22
29.2	0.04571	2.31	2.28
31.8	0.04417	2.37	2.39
33.5	0.04554	2.47	2.46
34.3	0.04630	2.52	2.50
36.2	0.04598	2.58	2.57
39.0	0.04719	2.71	2.68
46.2	0.04710	2.95	2.93
55.0	0.04656	3.20	3.21
68.5	0.04600	3.55	3.57
82.1	0.04538	3.86	3.87
96.1	0.04460	4.14	4.12
104.2	0.04314	4.24	4.24
126.0	0.04037	4.51	4.50
146.7	0.04750	4.69	4.69
165.5	0.03523	4.83	4.83
196.2	0.03199	5.01	5.00
223.2	0.02924	5.11	5.11
247.6	0.02731	5.20	5.19
266.6	0.02576	5.24	5.24
285.8	0.02439	5.28	5.30
296.7	0.02385	5.32	5.31

$$\chi' = 150 \times 10^{-6} \text{ cgsu.}$$

BEST AVAILABLE COPY

Table II. Infrared Bands and Assignments (in cm^{-1}) ^a

Absorption	Assignment
3200 br, s	$\nu(\text{OH})$
1815 sh, m	Sq, $\nu(\text{C}=\text{O})$
1640 sh, m	Sq, $\nu(\text{C}=\text{C})$
1500 br, s	Sq, $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$
1110, 1085 sh, w	Sq, ν_{13}, E_u ^b
850, 750 br, w	$\nu(\text{Fe}-\text{O}-\text{H}) + \rho_r(\text{H}_2\text{O})$
660, 460 br, w	$\rho_w(\text{H}_2\text{O})$
420 sh, w	unassigned
390 sh, w	$\nu(\text{Fe}-\text{O})$
350 sh, vw	Sq, ν_2, A_{1g} ^b

^a Abbreviations: br, broad; s, strong; sh, sharp; m, moderate; w, weak; v, very.

^b Ref 18.

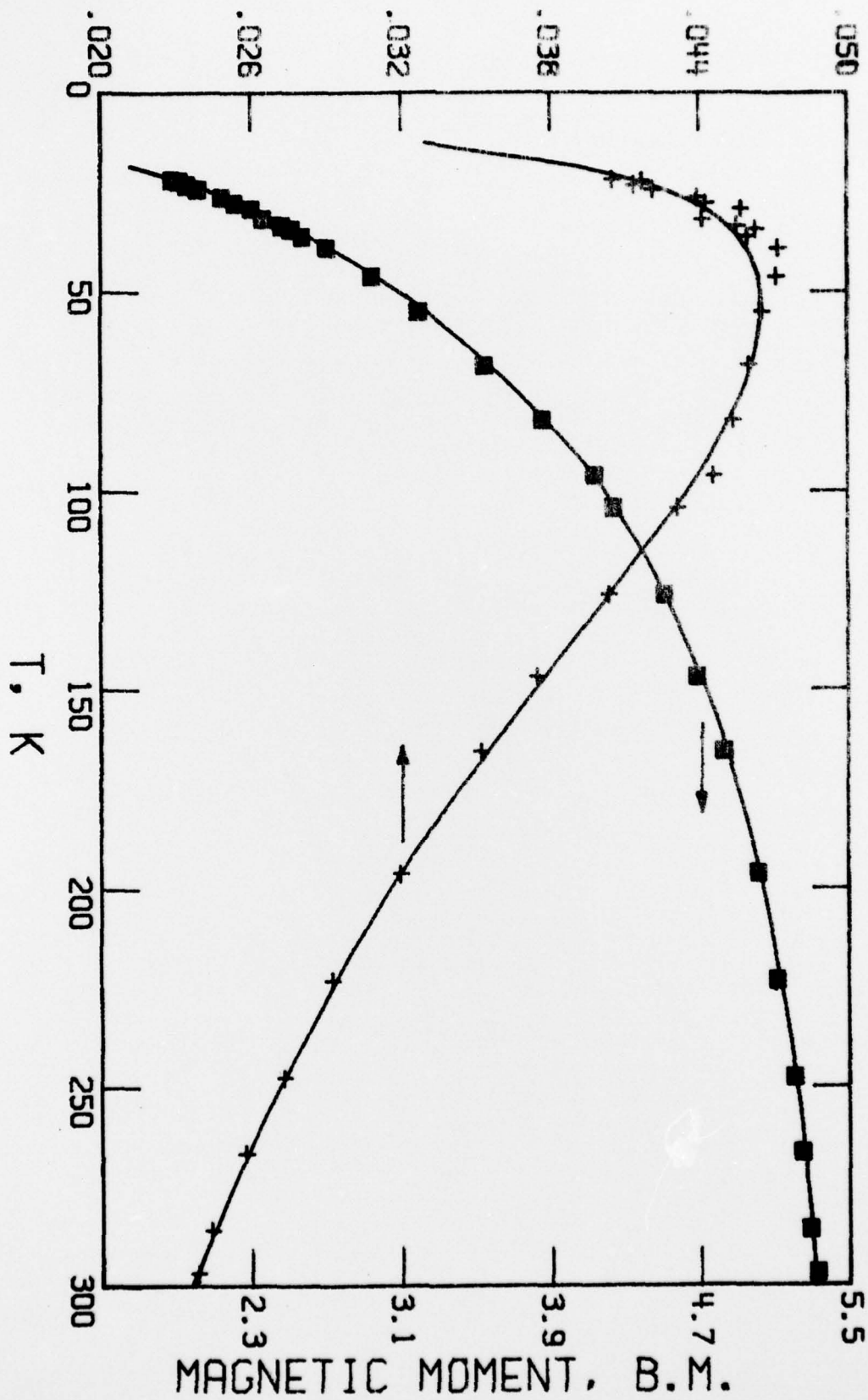
BEST AVAILABLE COPY

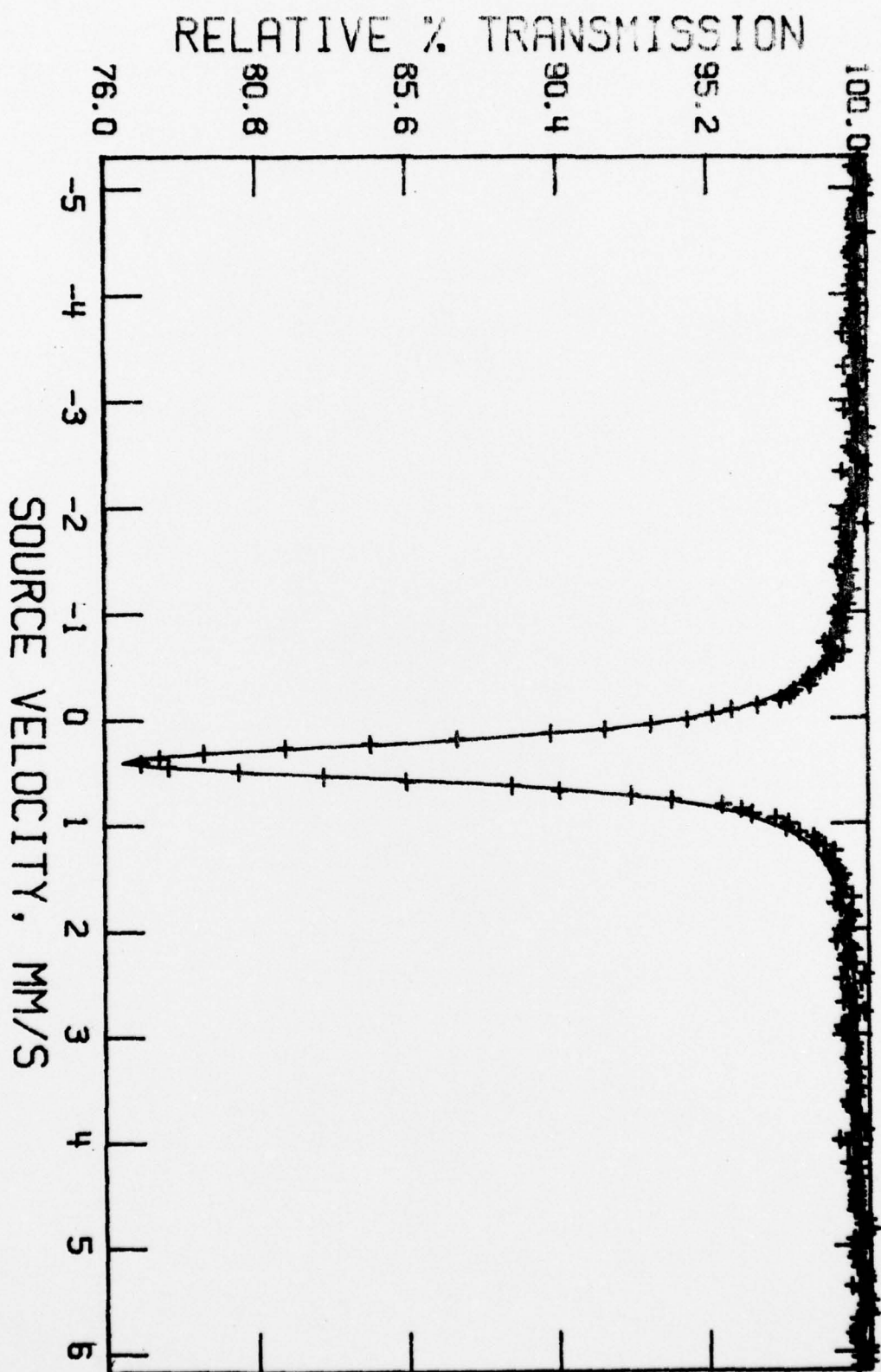
Figure Captions

Fig. 1 Effective magnetic moments for $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$. The solid line gives the theoretical moments obtained for an exchange-coupled $S_1=S_2=5/2$ dimer with $J = -6.9 \text{ cm}^{-1}$ and $g = 2.00$.

Fig. 2 Room temperature Mössbauer spectrum of $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$. The solid line gives the fit for a single Lorentzian line with parameters given in the text.

MOLAR SUSCEPTIBILITY





TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Office of Naval Research Arlington, Virginia 22217 Attn: Code 1021P 1	6	U.S. Army Research Office P. O. Box 12211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D. C. 20380	1
Director, Naval Research Laboratory Washington, D. C. 20390 Attn: Code 6100	1	Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D. C. 20360 Attn: Code 310C (H. Rosenwasser)	1		

TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. M. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia	22901 1	Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina	27514 1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas	77843 1	Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts	02139 1
Dr. C. Quicksall Georgetown University Department of Chemistry 37th & O Streets Washington, D.C.	20007 1	Dr. M. H. Chisholm Princeton University Department of Chemistry Princeton, New Jersey	08540 1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California	90024 1	Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts	02154 1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D. C.	20375 1	Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois	60201 1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee	37916 1	Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania	16802 1
Dr. A. Cowley University of Texas Department of Chemistry Austin, Texas	78712 1	Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma	73019 1