"acid stabilization" concept previously applied to the cadmium(I)[10] and gallium(I)[19] systems. The metal solubility in, or extent of reduction of, lead(II) and tin(II) salts increases about 30-fold when the anion is changed from chloride to tetrachloroaluminate, although this is still insufficient for stabilization of a solid product.

Dilution with solvent NaAlCl$_4$–AlCl$_3$, of course, reduces the total amount of metal solution per mole of solution. However, the mole fraction solubility based only on M^{2+} content [M/(M^{II} + M)] shows an interesting correlation with the proposed solute species on dilution from M(AlCl$_4$)$_2$ to the 5% solution. For a Cd$_2$$^{2+}$ product the equilibrium position ideally should not be dependent on dilution, as observed, whereas reduction of the dipositive cations to Pb$^+$ or Sn$_2$$^+$ (but *not* to the higher species) should increase on dilution, as observed. The actual change is about twice that expected for this simple treatment, suggesting a specific solvent effect. However, a quantitative argument regarding dilution effects is dangerous here, since it presumes proportional activity changes on dilution, such as Raoultian for Sn^{2+} or Pb^{2+} from 100 to 5% M(AlCl$_4$)$_2$ and the same Henry's law constant for the reduced ion throughout the dilution. Although this may not be an atrocious assumption, it is by no means assured.

An emf study of reduction of Ni^{2+} would be interesting in view of the substantial (9%) solution of the metal in molten NiCl$_2$.[20] However, investigations of this in the tetrachloroaluminate solvent were frustrated by the inability to obtain reasonable concentrations of NiCl$_2$ in NaAlCl$_4$, let alone to form solid Ni(AlCl$_4$)$_2$ (see Experimental Section). This is somewhat surprising in view of the known stability of Co(AlCl$_4$)$_2$,[21] but may be a result of the higher lattice energy of NiCl$_2$.

Synthetic work preliminary to the emf studies indicated the formation of MCl$_2$–2AlCl$_3$ compounds for tin and lead, the evidence being the totally unique powder patterns and the congruent melting points at this composition (see Experimental Section). For convenience these have been regarded herein as tetrachloroaluminates, an entirely reasonable but not established formulation. Recently, Belt and Scott[22] have reported X-ray powder data for some of the same systems but with somewhat different results. Our data for Sn(AlCl$_4$)$_2$ are in good agreement with theirs except that they appear to have included about five of the principal diffractions of AlCl$_3$. (The same spacings are also found in the data reported for a number of other systems.) However, their data for the PbCl$_2$–2AlCl$_3$ composition are in very poor agreement with those[15] obtained here. They also gave data reported to support the formation of a NiCl$_2$–AlCl$_3$ compound, contrary to our experience. Their data do not appear very conclusive, however, since at least 90% of the diffraction spacings given can be assigned to those of the original components. The reported green color is also at variance with either the yellow color of NiCl$_2$ observed for all solid systems or the rose to salmon colors of the very dilute melts. The use of "anhydrous" or dehydrated commercial reagents without further purification may have caused some difficulties in the earlier work.

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(20) J. W. Johnson, D. Cubicciotti, and C. M. Kelley, *J. Phys. Chem.*, **62**, 1107 (1958).

(21) J. A. Ibers, *Acta Cryst.*, **15**, 967 (1962).

(22) R. F. Belt and H. Scott, *Inorg. Chem.*, **3**, 1785 (1964).

Vibronic Polarization in the Electronic Spectra of Gillespite, a Mineral Containing Iron(II) in Square-Planar Coordination

By ROGER G. BURNS,[1] MICHAEL G. CLARK,[2] and ANTHONY J. STONE[2]

The polarized absorption spectra of iron in the mineral gillespite (BaFeSi$_4$O$_{10}$) have been measured in the region 4000–15,000 A. It has been shown that the spectra may be interpreted satisfactorily if it is supposed that the order of increasing energy of the 3d orbitals of the iron is d$_{z^2}$ < d$_{xz}$d$_{yz}$ < d$_{xy}$ < d$_{x^2-y^2}$. Approximate values for the energy separations of these orbitals in the high-spin configuration of the iron have been deduced. Vibronic polarization in the spectra of gillespite has been treated by the methods of group theory.

Introduction

Square-planar coordination by oxygen of ferrous iron is rare.[3] It is therefore of interest to examine the mineral gillespite, which is an example of this coordination.[4] The polarized absorption spectra in the region

(3) (a) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. 2, Oxford University Press, London, 1950, p 1347; (b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 711; (c) D. P. Mellor, *Chem. Rev.*, **33**, 179 (1943).

(4) A. Pabst, *Am. Mineralogist*, **28**, 372 (1943).

(1) University of California; address correspondence to the Department of Mineralogy and Petrology, University of Cambridge, Cambridge, England.

(2) University of Cambridge.

4000–15,000 A, the unpolarized infrared spectrum, and the magnetic susceptibility of gillespite have been measured.

Experimental Section

Polarized Absorption Spectra.—Spectral measurements were made by a microscope technique.[5] A thin section (0.0127 cm), cut from rock containing gillespite and mounted in transparent cement (Canada balsam), was placed on a three-axis universal stage attached to a polarizing microscope. A single crystal of gillespite was brought into the field of view of the microscope and, after a crystallographic or optical indicatrix axis had been identified by conventional methods, the microscope was mounted in the sample beam of a Cary Model 14 recording spectrophotometer. An identical microscope holding a glass slide containing only the transparent cement was placed in the reference beam of the spectrometer.

Infrared Spectra.—Qualitative spectral measurements were made in the region 8000–650 cm^{-1} using unpolarized radiation. The region 8000–3760 cm^{-1} was examined with a Cary Model 14 spectrophotometer, using finely ground gillespite in compressed KBr disks. Unicam SP 200 and Perkin-Elmer Infracord spectrophotometers were employed in the region 4000–650 cm^{-1}, using thick mulls of gillespite in hexachlorobutadiene or Nujol pressed into thin films between NaCl plates.

Magnetic Susceptibility Measurements.—The magnetic susceptibility of gillespite was measured in the range 77–300°K by the Gouy method. Measurements were also made at room temperature using both the Gouy and Faraday methods. All measurements were corrected for the diamagnetism of the material before calculating magnetic moments from bulk susceptibility data.

The Gillespite Crystal Structure

Gillespite is uniaxial (space group P4/ncc), with the pleochroic scheme $\vec{E} \perp c$, pale pink; $\vec{E} \parallel c$, deep rose-red (where $\vec{E}$ is the electric vector of the radiation).

The structure[4] contains [Si$_8$O$_{20}$] sheets, consisting of two linked sets of square groups of four [SiO$_4$] tetrahedra at two levels along the c crystallographic axis. Oxygen atoms occur in three kinds of positions. Two types (O$_I$ and O$_{II}$) bridge [SiO$_4$] tetrahedra, and the third (O$_{III}$) forms unshared vertices. Only the non-bridging O$_{III}$ type is coordinated to cations. Barium ions are in eightfold coordination with O$_{III}$ atoms belonging to two separate [Si$_8$O$_{20}$] sheets, and Fe^{2+} ions are in square-planar coordination with four O$_{III}$ atoms of one sheet. Fe–O internuclear distances are 1.97 A to the O$_{III}$ type and 3.98–4.75 A to the nearest O$_I$ and O$_{II}$ types. The Fe–O$_{III}$ distance is significantly smaller than the average Fe^{2+}–O distance in six-coordinated oxide and silicate structures, which is about 2.14 A.[6] The square-planar [FeO$_4$] group is perpendicular to the c axis. The nearest atoms vertically above and below Fe^{2+} are other Fe^{2+} ions at 8.025 A along the c axis.

Results

All measurements were performed on a gillespite specimen from Fresno County, Calif.

The axial, σ, and π polarized spectra[7,8] were recorded, and of these the axial and σ spectra were found to be identical. This shows that the spectra are due to

electric dipole transitions because the axial and σ spectra have the same orientation of the electric vector ($\vec{E} \perp c$) but different orientations of the magnetic vector.

The spectra are illustrated in Figure 1, and data on the absorption maxima are summarized in Table I.
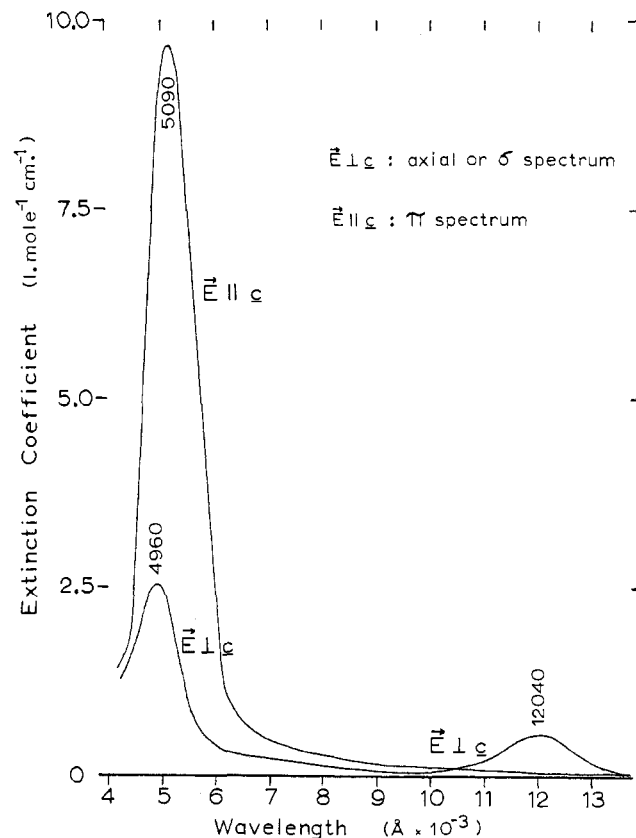

Figure 1.—The polarized absorption spectra of gillespite.

TABLE I
ABSORPTION MAXIMA IN THE POLARIZED SPECTRA OF GILLESPITE

Spectrum	Orientation of electric vector	Position of band, cm^{-1}	Extinction coeff, l. mole^{-1} cm^{-1}
Axial and σ	$\vec{E} \perp c$	20,160	2.55
Axial and σ	$\vec{E} \perp c$	8,300	0.6
π	$\vec{E} \parallel c$	19,650	9.8

No absorption bands were observed in the infrared spectrum between 8000 and 3760 cm^{-1}, in agreement with observations on the reflectance spectrum.[9]

There is a weak band at 3450 cm^{-1} in the O–H stretching region, which is attributed to the small water impurity in the specimen. (A water analysis yielded $H_2O(+) = 0.03$ wt %, $H_2O(-) = 0.03$ wt %.) Detailed analysis of this band could yield information on the mechanism of leaching of gillespite.[4]

There is a region of intense absorption below 2000 cm^{-1}, with maximum absorption at about 1000 cm^{-1}. Some partly resolved structure was observed in this region.

The results of the temperature study of the magnetic

(5) R. G. Burns, *J. Sci. Instr.*, **43**, 58 (1966).

(6) R. G. Burns, Ph.D. Thesis, University of California, Berkeley, Calif.

(7) E. V. Sayre, K. Sancier, and S. Freed, *J. Chem. Phys.*, **23**, 2060 (1955).

(8) D. S. McClure, *Solid State Phys.*, **9**, 437 (1959).

(9) D. Goodgame, private communication.

susceptibility of gillespite were fitted by least squares to the equation $1/\chi_{Fe} = \alpha T + \beta$, where χ_{Fe} is the susceptibility per formula weight, corrected for diamagnetism, and T is the absolute temperature.

The values obtained for α and β were 0.3074 ± 0.0031 and 0.0443 ± 0.643, respectively.

Thus there is no significant change of magnetic moment with temperature. The actual value for the magnetic moment of the iron, obtained from α, is 5.12 $\pm$ 0.05 BM. The room-temperature measurements gave values which agreed with this result to within experimental error.

Interpretation of Spectra

The spectra of gillespite may be interpreted by using group theoretical selection rules. Only symmetry considerations are applied in this treatment, which means that it is not necessary to assume an ionic model for the bonding of Fe^{2+} in the gillespite structure.

The point symmetry of the crystallographic position occupied by Fe^{2+} in the gillespite structure is C_4.[4,10] This symmetry represents the over-all environment about the Fe^{2+} ion. Since the second nearest neighbors are oxygen atoms situated more than twice as far from the Fe^{2+} as the four nearest neighbors, it is reasonable to consider only the planar [FeO$_4$] unit. The symmetry of the electronic environment of Fe^{2+} is then D_{4h}.

There is a possible ambiguity in the definition of the diad axes in this group; we take x and y parallel to the two O_{III}–Fe–O_{III} axes and use the character table given by Cotton.[11]

The magnetic moment indicates that the Fe^{2+} ion has four unpaired electrons in the gillespite structure. The observed value is slightly higher than the "spin-only" value (4.9 BM).

The constancy of the magnetic moment over the temperature range 77–300°K indicates that thermal population of excited states is negligible, at least up to 300°K. This is supported by Mössbauer measurements, which indicate that the quadrupole splitting of the Fe^{2+} resonance spectrum of gillespite is independent of temperature,[12] apart from the small temperature variations due to other factors such as the thermal expansion of the lattice. Thus there is evidence that the first excited state is at least 500 cm^{-1} above the ground state.

The d_{z^2} orbital or the degenerate $d_{xz}d_{yz}$ pair of orbitals will lie lowest in energy, because these have the least repulsive electrostatic interaction with ligand orbitals. Similarly, the $d_{x^2-y^2}$ orbital lies highest in energy and the d_{xy} lies next highest. The electronic configurations of the two possible ground states are shown in Figures 2a and b. The states are $^5A_{1g}$ and ^5E_g, respectively, and are shown, together with the excited states considered, in Figures 2c and d. The state $^5B_{2g}$ corresponds to the configuration $d^1_{z^2}d^1_{xz}d^1_{yz}d^2_{xy}d^1_{x^2-y^2}$, and the state
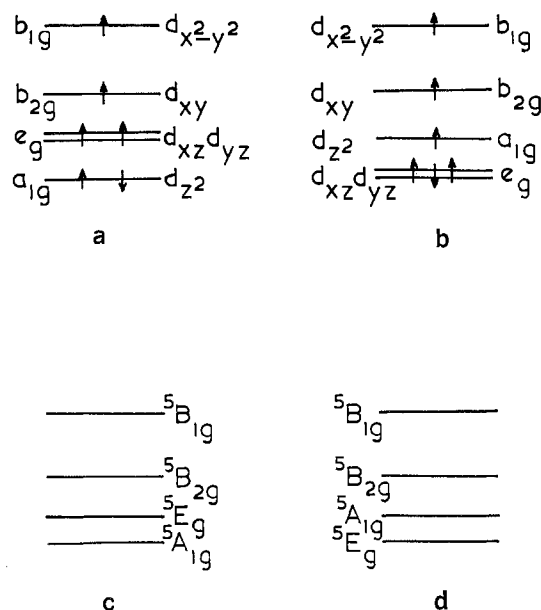

Figure 2.—Energy level diagrams for 3d orbitals and electronic states for Fe^{2+} in gillespite. (a) Electronic configuration of the ground state if d_{z^2} orbital is the most stable. (b) Electronic configuration of the ground state if $d_{xz}d_{yz}$ orbital pair is the most stable. (c) Electronic states corresponding to the ground state of Figure 2a. (d) Electronic states corresponding to the ground state of Figure 2b.

$^5B_{1g}$ to $d^1_{z^2}d^1_{xz}d^1_{yz}d^1_{xy}d^2_{x^2-y^2}$. The symmetry species of these states may be written down immediately when it is noted that the half-filled shell $d^1_{z^2}d^1_{xz}d^1_{yz}d^1_{xy}d^1_{x^2-y^2}$ has symmetry A_{1g}.

The polarized spectra indicate that electric dipole transitions are involved, and their relatively low intensity and position in the spectrum suggest d → d transitions. However, simple d → d transitions are g → g transitions and therefore are forbidden by the Laporte selection rule. Transitions may be allowed by vibronic coupling, that is, simultaneous excitation of a u vibrational mode. The symmetries of the normal modes[13] of the [FeO$_4$] unit are found to be $A_{1g} + A_{2u} + B_{1g} + B_{2g} + B_{2u} + 2E_u$. Allowed transitions to excited quintet states from the two possible ground states (see Figures 2c and d) have been deduced,[11] assuming simultaneous excitation of one normal vibration from its ground state to its first excited state. The results are summarized in Table II.

The energy ΔE_{obsd} of the observed transition is related to the energy separation ΔE_{el} of the vibrationally unexcited states and the fundamental vibrational frequency ν of the normal mode allowing the transition by the equation $\Delta E_{obsd} = \Delta E_{el} + h\nu$, where h is Planck's constant.

A comparison of the polarized spectra (Figure 1) with the predicted transitions (Table II) reveals that the best correlation exists for the $^5A_{1g}$ ground state. If ^5E_g were the ground state, the allowed transitions $^5E_g \rightarrow$ $^5B_{2g}$ and $^5E_g \rightarrow$ $^5B_{1g}$ should result in two absorption bands in each polarized spectrum, whereas the π spectrum contains only one band. The presence of an

(10) "International Tables for X-Ray Crystallography," Vol. I, the Kynoch Press, Birmingham, England, 1952, p 225.

(11) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers Ltd., London, 1964.

(12) M. Bancroft, private communication.

(13) In a similar calculation in ref 11, B$_{1u}$ should read B$_{2u}$ if the axes of Figure 8.14, p 234, are used.

TABLE II

Ground state	Polarization of electric vector	Transition	Normal modes allowing vibronic coupling	Assignment
$^5A_{1g}$	$\vec{E} \parallel c$	$A_{1g} \rightarrow E_g$	E_u	*Ca.* 1000 cm^{-1}
		$A_{1g} \rightarrow B_{2g}$	None	Forbidden
		$A_{1g} \rightarrow B_{1g}$	B_{2u}	19,650 cm^{-1}
$^5A_{1g}$	$\vec{E} \perp c$	$A_{1g} \rightarrow E_g$	$A_{2u} + B_{2u}$	*Ca.* 1000 cm^{-1}
		$A_{1g} \rightarrow B_{2g}$	E_u	8,300 cm^{-1}
		$A_{1g} \rightarrow B_{1g}$	E_u	20,160 cm^{-1}
^5E_g	$\vec{E} \parallel c$	$E_g \rightarrow A_{1g}$	E_u	Inconsistent with observed spectra
		$E_g \rightarrow B_{2g}$	E_u	
		$E_g \rightarrow B_{1g}$	E_u	
^5E_g	$\vec{E} \perp c$	$E_g \rightarrow A_{1g}$	$A_{2u} + B_{2u}$	
		$E_g \rightarrow B_{2g}$	$A_{2u} + B_{2u}$	
		$E_g \rightarrow B_{1g}$	$A_{2u} + B_{2u}$	

absorption band in the 12,000-A region in the axial spectrum and its absence in the π spectrum may be explained by the $^5A_{1g} \rightarrow {}^5B_{2g}$ transition, which is allowed only when the electric vector is perpendicular to the *c* axis.

There are other reasons against ^5E_g as the ground state. Firstly, if ^5E_g were the ground state, it would be unstable with respect to a Jahn–Teller distortion splitting the degeneracy of the $d_{xz}d_{yz}$ orbital pair. This degeneracy can only be split if the over-all environment about Fe^{2+} has no symmetry axes of order greater than 2. Obviously, the C_4 symmetry of the crystallographic position occupied by Fe^{2+} in the gillespite structure[4,10] does not fulfill this criterion. Thus the crystal structure shows no evidence of the Jahn–Teller distortion which might be expected if Fe^{2+} were in a ^5E_g ground state. However, any Jahn–Teller distortion which did occur might be too small to be observable, because the orbitals involved, *i.e.*, the $d_{xz}d_{yz}$ pair, do not interact very strongly with the ligand orbitals.

Secondly, if ^5E_g were the ground state, a large contribution to the magnetic moment from the orbital angular momentum would be expected, whereas no first-order contribution is expected for the $^5A_{1g}$ state. In fact, the observed magnetic moment is only slightly greater than the "spin-only" value. The small difference will presumably be due to spin–orbit coupling effects.

Assuming $^5A_{1g}$ to be the ground state of the Fe^{2+}, the absorption bands observed in the polarized spectra (Figure 1) are assigned to specific transitions in the last column of Table II. The $^5A_{1g} \rightarrow {}^5E_g$ transition was not observed, but it is expected to occur at a wavelength longer than those for which polarized spectral measurements were made. Presumably it lies in the region of intense absorption around 1000 cm^{-1} in the unpolarized infrared spectrum. However, vibrational modes associated with the silicate sheet structures also occur in this region.[14]

It is observed that the band assigned to the $^5A_{1g} \rightarrow {}^5B_{1g}$ transition differs in intensity and frequency in the two polarized spectra. The frequency shift represents

the difference in energy of the fundamental frequencies of the vibrational modes involved, assuming that a single vibrational quantum is involved in each case

$$\nu_{E_u} - \nu_{B_{2u}} = 20,160 - 19,650 = 510 \text{ cm}^{-1}$$

Since E_u vibrations are in-plane distortions of the [FeO$_4$] square, while the B_{2u} mode is a bending of the square, it is reasonable that $\nu_{E_u} > \nu_{B_{2u}}$. The oxygens of the [FeO$_4$] unit are part of an [Si$_8$O$_{20}$] sheet, and vibrations of the [FeO$_4$] square must be regarded as vibrations of a silicate sheet, modified by the Fe^{2+} ion. The frequencies ν_{E_u} and $\nu_{B_{2u}}$ may be estimated from infrared spectral measurements of micas[14] to be: ν_{E_u} 1000 $\pm$ 250, $\nu_{B_{2u}}$ 600 $\pm$ 250 cm^{-1}. These estimates are consistent with the observed value of $\nu_{E_u} - \nu_{B_{2u}}$.

The $^5A_{1g} \rightarrow {}^5E_g$ transition, expected to occur at about 1000 cm^{-1} in the infrared region, also relies on different vibrational modes in the vibronic coupling mechanism for the two orientations of the electric vector (Table II). If the absorption peaks corresponding to $^5A_{1g} \rightarrow {}^5E_g$ could be identified in the polarized infrared spectra, they would show wavelength shifts analogous to those observed for the $^5A_{1g} \rightarrow {}^5B_{1g}$ transition.

The difference in intensity with change in polarization, observed in the $^5A_{1g} \rightarrow {}^5B_{1g}$ transition, may be rationalized by noting[15] that vibronic coupling may be regarded as causing small amounts of excited electronic states to be mixed into the states involved in the transition. In this case the most important contributions are likely to be mixing of the $4p_z$ orbital into the $3d_{x^2-y^2}$ orbital by the B_{2u} vibration (π spectrum) and mixing of the $4p_x4p_y$ orbitals into the $3d_{x^2-y^2}$ orbital by the E_u vibration (σ spectrum). With this simplification, the intensity is proportional to

$$\frac{1}{E_1^2} \frac{h}{4\pi\nu} M^2$$

where M is a factor consisting of matrix elements which express the geometrical factors determining how efficiently the vibration mixes in the excited states, ν is the frequency of the vibration, and E_1 is the energy of the excited state above that of the state it contaminates.

Now $\nu_{E_u} \cong 2\nu_{B_{2u}}$, and furthermore the ligand field will cause the $4p_z$ orbital to be at a lower energy than the $4p_x4p_y$ orbital pair. Thus, because of the $(E_1^2\nu)^{-1}$ factor, the π-polarized band is expected to be at least four times as intense as the σ-polarized one. On the other hand, the factor M^2 is likely to act in the opposite direction, being larger for the σ band. The difficulties involved in calculating M mean that it is very difficult to obtain an accurate theoretical estimate of the ratio of intensities.[15] However, it seems that the observed ratio of 3.8 is reasonable.

For spin pairing in octahedral complexes of Fe^{2+} a Δ value of about 20,000 cm^{-1} is required.[16,17] Also, for

(14) W. Vedder, *Am. Mineralogist*, **49**, 736 (1064), and references therein.

(15) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 297.

(16) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 9753 (1954).

(17) See ref 15, p 266.

a given over-all energy separation of the d orbitals, the orbital energy stabilization achieved by spin pairing is considerably less in the square-planar case than in the octahedral case. Since it is observed that in gillespite all the 3d orbitals lie within a range of 20,000 cm^{-1}, the observation that the ferrous ion in gillespite is in a high-spin state is exactly what one would expect.

Conclusions

The electronic spectra of gillespite are consistent with the ground state of Fe^{2+} in the gillespite structure being $^5A_{1g}$, corresponding to the configuration $d^2_{z^2}d^1_{xz}d^1_{yz}d^1_{xy}d^1_{x^2-y^2}$. The transitions observed may be assigned to electronic transitions from the $^5A_{1g}$ state to other quintet states of the Fe^{2+}, occurring by the mechanism of vibronic coupling.

The first excited state, ^5E_g (corresponding to $d^1_{z^2}(d_{xz}d_{yz})^3d^1_{xy}d^1_{x^2-y^2}$), appears to lie between 500 and 1500 cm^{-1} above the $^5A_{1g}$ ground state. The remaining quintet excited states, $^5B_{2g}$ ($d^1_{z^2}d^1_{xz}d^1_{yz}d^2_{xy}d^1_{x^2-y^2}$) and

$^5B_{1g}$ ($d^1_{z^2}d^1_{xz}d^1_{yz}d^1_{xy}d^2_{x^2-y^2}$), lie approximately 7500 and 19,000 cm^{-1} above the ground state, respectively. These energies are estimates of the energies of vibrationally unexcited states, based on the estimates of vibrational frequencies made above.

Electron Spin Resonance of Pentamethylenetetrazole Manganese(II) and Copper(II) Complexes[1]

By HENRY A. KUSKA,[2a] FRANK M. D'ITRI,[2b] and ALEXANDER I. POPOV[2b]

Electron spin resonance spectra of the pentamethylenetetrazole (PMT) complexes Mn(PMT)$_6$(ClO$_4$)$_2$, Cu(PMT)$_6$(ClO$_4$)$_2$, and Cu(PMT)$_4$(ClO$_4$)$_2$ were obtained. For Mn(PMT)$_6$(ClO$_4$)$_2$ complex dispersed in Zn(PMT)$_6$(ClO$_4$)$_2$ the data indicate that the metal–ligand bonds are highly ionic (91%) and that the distortion from octahedral symmetry ($D = 41 \times 10^{-4}$ cm^{-1}) is small. For Cu(PMT)$_4$(ClO$_4$)$_2$ and Cu(PMT)$_6$(ClO$_4$)$_2$ it was possible to obtain high-resolution spectra of the copper nuclear splittings from the undiluted powder. Nitrogen superhyperfine splittings were observed in dilute solid solutions of Cu(PMT)$_6$(ClO$_4$)$_2$. The Cu(PMT)$_6$(ClO$_4$)$_2$ data indicate that the Jahn–Teller distortion resonates along the three equivalent octahedral axes at room temperature when the compound is in a suitable diamagnetic host, but in the undiluted powder the compound has a permanent tetragonal distortion. The copper PMT complexes are approximately 80% ionic. The bonding of the PMT ligand appears to be similar to that of pyridine with the PMT nitrogen slightly less basic than the pyridine nitrogen in 4-cyanopyridine.

Introduction

Tetrazoles are five-membered, heterocyclic ring compounds which contain one carbon and four nitrogen atoms linked by three single and two double bonds. The parent compound may exist in tautomeric forms I and II.[3] It is found that 97% of a mixture of I and
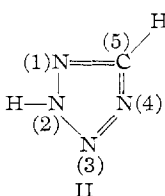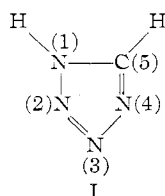
I exists in the form I.[4]

The tetrazole ring is unusual among cyclic systems in that it offers only two points of substitution—in positions 1 or 2 and 5. Pentamethylenetetrazole, III (hereafter abbreviated as PMT), represents a special group of dialkyl-substituted tetrazole derivatives in which the two alkyl substituents form a second cyclic system.
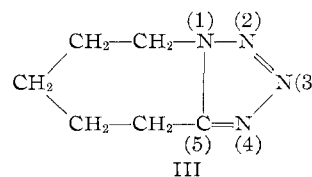
(1) Presented before the 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 31, 1966.

(2) (a) The University of Akron; (b) Michigan State University.

(3) D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **82**, 5007 (1960).

(4) J. B. Lounsbury, *J. Phys. Chem.*, **67**, 721 (1963).