80–90% of the sample weights, with oxygen only 0.25 to 1.5% in four products analyzed by neutron activation analysis.

Because of the possibility that the Si–S mixture could react with the pyrophyllite (a hydrated aluminum silicate) sample containers under extreme conditions, we also carried out reactions in boron nitride tetrahedrons. The same glassy products were obtained in the latter, and we thus believe that, in spite of the poor analysis, the glasses contain essentially silicon and sulfur. Oxidation of these glasses in air begins at 425° as shown by initial weight loss in TGA and the beginning of a large exotherm in differential thermal analysis. Preliminary density measurements yielded 2.07 ± 0.02 g./cc.

The most remarkable property of these glassy products is their hydrolytic stability, which is much greater than that of normal silicon mono- and disulfides. Even with finely ground material, reaction with water to give H_2S and amorphous silica took many hours to complete, compared to minutes for the normal sulfide, or even less for the monosulfide. We prepared samples of the latter by passing CS_2 over hot Si in a quartz tube at 1000° according to a procedure previously described.[7] The solid condensate obtained was mainly a fluffy pale yellow powder which was pyrophoric when dropped onto water. Careful examination of the quartz reaction tube revealed a small amount of orange, transparent glass similar in appearance to some of the high pressure products. This was amorphous in X-ray examination and also of much greater hydrolytic stability than the normal silicon sulfides. Hydrolysis of this glass, however, gave a soft, white material quite different in appearance from the tan, grainy residue obtained on hydrolysis of the high pressure glass.[8]

A second crystalline silicon sulfide occurred as gray needle-like crystals radiating toward the center of the product. The X-ray diffraction powder pattern characteristic of this product (Table I, column (b)) was obtained in about 20 runs. Preliminary attempts to index this powder pattern yielded several sets of tetragonal lattice constants which gave fair agreement with observed $\sin^2 \theta$ values. We hope the structure of this compound can be resolved by a single crystal X-ray study. Many products containing this material were heterogeneous, but it could be obtained in good yield from approximately 1Si:2S mixtures held at 45 kbars and 1100° for 5 min. Microscopic observation of its hydrolysis showed it to be similar to that of normal SiS_2.

A dull, opaque, hard bronze to tan solid that reacted vigorously in water was found in various amounts in 12 runs. It was the major product from Si–S mixtures held 5 min. at 44 kbars and 1400°. The strongest lines in its X-ray diffraction powder pattern are listed in Table I, column (c).

Acknowledgment.—We thank Dr. W. Clavan and Mr. R. Hamilton for obtaining the X-ray patterns and the Pennsalt analytical and shop groups for their help in this work. It was supported in part by the Office of Naval Research.

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(7) R. F. Barrow and W. Jevons, *Proc. Roy. Soc.* (London), **A169**, 46 (1939).

(8) Barrow and Jevons[7] reported glassy products from vacuum sublimation of the monosulfide. They found that the band spectra of vapor from glasses and the yellow monosulfide powder were the same.

Correspondence

Hydrogen Bonding to Manganese(III) β-Ketoenolates: Influence on the Low Energy Electronic Band

Sir:

The visible and near-infrared region of the spectra of manganese(III) acetylacetonate, $Mn(AA)_3$, and other β-ketoenolate compounds of this ion is known to contain two bands of comparable intensity.[1–5] The recent publication by Morosin and Brathovde[6] of the X-ray crystal structure of $Mn(AA)_3$ prompts us to communicate some of our findings with regard to the spectral properties of β-ketoenolates of manganese(III), particularly since the most recently proposed[2,5] assignment can now be ruled out, while an earlier one[3,4] has several features suggesting it to be incorrect also.

In high-spin $3d^4$ complexes with O_h symmetry, one expects a ^5E_g ground state with single spin-allowed crystal-field transition to the $^5T_{2g}$ level. Lowering the symmetry to D_3 does not remove the degeneracy of the ground state but does split[3,5] the $^5T_{2g}$ state. This splitting has been observed by Piper and Carlin[3] in polarized spectral studies.

Since Morosin and Brathovde[6] have found that crystalline $Mn(AA)_3$ contains six Mn–O bonds of essentially equal length and that the molecule as a whole is only slightly distorted from the structure observed[7] for $Fe(AA)_3$, spectral assignments must be made within the crystal-field framework of an octahedral configuration with a rhombic perturbation. The above authors[6] have discussed the implications of the structure of $Mn(AA)_3$ on the question of Jahn–Teller distortion,

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(1) J. P. Fackler, Jr., and I. D. Chawla, *Inorg. Chem.*, **3**, 1130 (1964).

(2) R. Dingle, *J. Mol. Spectry.*, **9**, 426 (1962).

(3) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

(4) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962).

(6) B. Morosin and J. R. Brathovde, *Acta Cryst.*, **17**, 705 (1964).

(7) R. B. Roof, Jr., *ibid.*, **9**, 781 (1956).

TABLE I

VISIBLE AND NEAR-INFRARED BANDS OF MANGANESE(III) β-KETOENOL COMPLEXES

β-Diketone	pK_a[a]	Av. position in Cu(II)[b] × 10^3 cm.$^{-1}$	Manganese(III)[c] × 10^3 cm.$^{-1}$, ε in paren.
$(CF_3CO)_2CH_2$	4.35	14.5	~18.7 (240); ~18.0^R 11.6 (89); 9.4^R
$(CH_3CO)_2CHCN$	4.40	15.4	~17.5 $(270)^B$ 8.06 $(100)^B$
$(CF_3CO)(CH_3CO)CH_2$	6.40	. . .	17.2 (190); ~17.9^R 9.00 (95); 7.7^R
$(CH_3CO)_2CH_2$	10.50	16.3	~17.9 (200) 9.52 (110)
$[(CH_3)_2CHCO]_2CH_2$	12.48	16.4	~17.9 (200) 8.85 (105)
$(CH_3CO)_2CHCl$	. . .	16.7	~17.0 8.50
$[(CH_3)_3CCO]_2CH_2$	14.48	16.8	~17.9 (200); ~17.9^R 8.70 (110); 8.0^R

[a] 75% dioxane–water, G. S. Hammond, W. G. Borduin, and G. A. Guter, *J. Am. Chem. Soc.*, **81**, 4682 (1959); A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1952. [b] Average position of bands IV and V, ref. 8 and 9. [c] Cyclohexane solvent except B, benzene, and R, diffuse reflectance.

specifically as related to its infrared spectrum. However, they have not implied what effect this structure determination has on the proposed electronic[1-5] assignments.

The assignment of Dingle[2] suggesting that the 9000 cm.$^{-1}$ band in $Mn(AA)_3$ arises from a transition within the ^5E component split by a "tetragonal perturbation of the regular D_3 complex" clearly is incorrect. Jørgensen's assignment[5] suffers the same fate since the $^5T_{2g}$ state certainly is not split by 9000 cm.$^{-1}$.

The arguments Dingle has used against assigning the low-energy band to a $^5E_2 \rightarrow {}^3T_1$ spin-forbidden transition are valid and have been confirmed by us (Table I). Using either the acidity of the β-ketoenol ligand (a tenuous correlation subject to considerable uncertainty) or the position of the visible bands in the spectra of the copper complexes[8,9] as an estimate of relative Dq values, the position of the low-energy band cannot be predicted using a Tanabe–Sugano[10] diagram. Also the intensity of the low-energy band appears to be comparable with the intensity of the band near 20,000 cm.$^{-1}$, particularly in reflectance (Figure 1). It is extremely difficult to rationalize these facts[3] if one is to assume that the low-energy band is a spin-forbidden transition.

We have found that the low-energy band in the tris-β-ketoenolates of manganese(III) is strongly perturbed by hydrogen-bonding solvents. Spectra for manganese(III) diisobutyrylmethane, $Mn(DIBM)_3$, a normal, high-spin β-ketoenolato complex of manganese(III) with considerable solubility in most organic solvents, are presented in Figure 1. The hypsochromic shift and decrease in intensity of the band which is indicated cannot be due to dissociation of the complex with subsequent coordination by the solvent as acetonitrile or pyridine would produce a larger effect than *n*-butyl or methyl alcohol. Furthermore, *chloroform produces a pronounced shift* while it certainly is not expected to coordinate with the metal. It is noted that the 18,000 cm.$^{-1}$ band is not influenced strongly by the solvent changes.

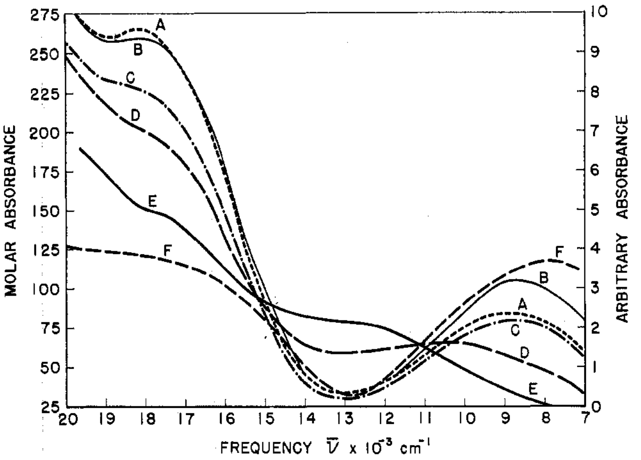

Figure 1.—Absorption spectra of tris(2,6-dimethyl-3,5-heptanediono)manganese(III) in various solvents: A, acetonitrile with and without added pyridine; B, cyclohexane; C, *t*-butyl alcohol; D, *n*-butyl alcohol; E, methyl alcohol; F, reflectance.

The change in the C–D stretching frequency which occurs when $Mn(DIBM)_3$ is dissolved in a $CDCl_3$–CCl_4 mixture (Figure 2) clearly shows bond formation between $CDCl_3$ and the complex. The splitting that occurs is qualitatively in the proper direction and is of correct magnitude for a normal deuterium bond of $CDCl_3$ with oxygen bases. This finding suggests that hydrogen-bond formation may have a larger effect on the solvent extraction of β-ketoenol complexes than Hopkins and Douglas thought likely in their recent paper.[11]

The shifts observed in the low-energy band of $Mn(DIBM)_3$ can be rationalized if one admits the possibility of low-energy "charge transfer." The calculations of Barnum[4] have suggested that the π_3 ligand level in tris-β-ketoenolates occurs near the t_{2g} level of the $3d^n$ metals (in O_h). Since the $\pi_3 \rightarrow \pi_4^*$ transition appears near 35,000 cm.$^{-1}$ and since the $t_{2g} \rightarrow e_g^*$ transition appears at ~18,000 cm.$^{-1}$, a transition from e_g^* to π_4^* might reasonably appear in the visible or near-infrared. The band intensity presumably could be modified by the energy and the symmetry of the transition. Such a transition might be perturbed considerably by solvent interaction with the chelate ligand.

An alternate "charge-transfer" possibility exists since a nonbonding set of electrons occur on the β-ketoenol oxygens. A transition from a filled nonbonding orbital on oxygen to the partially filled e_g^* or t_{2g} orbitals (in O_h) on manganese(III) could conceivably occur in the

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(8) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

(9) J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **2**, 102 (1963).

(10) See, for example, T. M. Dunn in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 249.

(11) P. D. Hopkins and B. E. Douglas, *Inorg. Chem.*, **3**, 357 (1964).

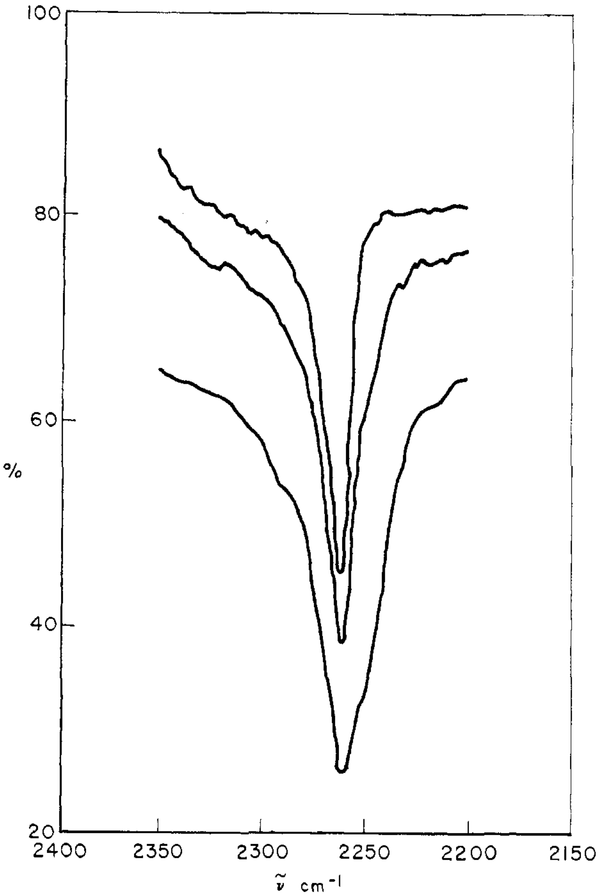

Figure 2.—Infrared C–D band of $CDCl_3$ in CCl_4 with added $Mn(DIBM)_3$: upper curve, no $Mn(DIBM)_3$, ~10% $CDCl_3$; middle curve, $CDCl_3$ to Mn(III) ratio ~10; lower curve, $CDCl_3$ to $Mn(DIBM)_3$ ratio ~2.5.

visible or near-infrared. Hydrogen-bonding solvents might be expected to perturb such a transition strongly through interaction with the oxygens, increasing the energy of the transition.

The size of the β-ketoenol ligand used in this study suggests a bulky solvent has some difficulty approaching closely to hydrogen bond with the ligands. When *n*-butyl and *t*-butyl alcohols are compared (Figure 1) a steric effect appears to be operative. Studies are currently in progress to observe the extent of the hydrogen-bond formation between various β-ketoenolates and several hydrogen-bonding solvents. For example, in the infrared only H-bonded OH is observed when $Mn(DIBM)_3$ is added to CCl_4 initially saturated with H_2O. In fact, CCl_4 solutions containing $Mn(DIBM)_3$ take up considerably more water than is dissolved without the complex being present. Also, infrared studies of $Co(AA)_3$, $Cr(AA)_3$, $Fe(AA)_3$, and $Be(AA)_2$ in $CDCl_3$ show these complexes, too, D-bond to the $CDCl_3$.

Chemical evidence suggests low energy "charge transfer" to be feasible in manganese(III) β-ketoenolates. 3-Chloroacetylacetone appears to reduce manganese(III). The tris chelate extracted into hexane decomposes with a half-life which appears to be of less than 15 min. duration. $Mn(AA)_3$ long has been known to decompose in the presence of light[3] and the hexafluoroacetylacetone and 3-cyano-2,4-pentanedione derivatives cannot be prepared by the usual oxidative procedures from manganese(II). The former complex appears to decompose when moist, the manganese being reduced in the process.

At this time it is unknown whether the hydrogen-bond interaction between the solvent and the complex involves primarily the chelate oxygens or the chelate ring itself. The oxygens certainly are basic, as indicated by the polymerization of nickel(II) and cobalt(II) acetylacetonates.[12] However, interaction between silver ion[13] and the chelate rings and bond formation by platinum[14] to the α-carbon suggests the ring itself (or the α-carbon) may be basic enough to form hydrogen bonds. Benzene is known to form weak hydrogen bonds[15] to $CHCl_3$. The extent of hydrogen-bond formation between complexes of β-ketoenols generally and various solvents is not yet known, but it is believed that this possible interaction has been badly neglected and may lead to considerable re-evaluation of data, particularly for studies conducted in $CHCl_3$ or MeOH.[16]

Acknowledgments.—The support of the National Science Foundation is gratefully acknowledged.

[12] See, for example, J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963), and refer ences therein.

[13] C. H. Oestreich, Ph.D. Thesis, Ohio University, 1961.

[14] A. G. Swallow and M. Truter, *Proc. Roy. Soc.* (London), **254**, 205 (1960).

[15] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).

[16] F. R. Clark, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964).

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Paratungstate Ion

Sir:

No general principle has yet been noted for the structures of the several isopoly- and heteropolyanions: $Nb_6O_{14}^{-8}$ and $Ta_6O_{14}^{-8}$,[1,2] $Mo_7O_{24}^{-6}$ and $Mo_8O_{26}^{-4}$,[3-5] $TeMoO_{24}^{-6}$,[6,7] $V_{10}O_{28}^{-6}$,[8-10] $MnMo_9O_{32}^{-6}$,[11] $W_{12}O_{40}^{-8}$,[12] $W_{12}O_{46}^{-20}$,[13] $PW_{12}O_{40}^{-3}$,[12,14] and $P_2W_{18}O_{62}^{-6}$.[14] Aside from tetrahedral coordination around P in the two phosphotungstate ions, all of these structures are based

[1] I. Lindqvist, *Arkiv Kemi*, **5**, 247 (1953).

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[5] I. Lindqvist, *Acta Chem. Scand.*, **4**, 551 (1950); *Arkiv Kemi*, **2**, 349 (1950).

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[10] H. T. Evans, Jr., A. G. Swallow, and W. H. Barnes, *J. Am. Chem. Soc.*, **86**, 4209 (1964).

[11] J. L. T. Waugh, D. P. Shoemaker, and L. Pauling, *Acta Cryst.*, **7**, 438 (1954).

[12] J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); also J. F. Keggin, *Proc. Roy. Soc.* (London), **A144**, 75 (1934).

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[14] B. Dawson, *ibid.*, **6**, 113 (1953).