zinc(II), tetrahedral coordination of the metal is realized.[9]

Independent work in each of our laboratories has resulted in the preparation and characterization of bis(dipivaloylmethanido)iron(II), $Fe(DPM)_2$. This bright yellow material, which chars immediately on exposure to air, is isomorphous[9] with the tetrahedral (strictly D_{2d}) $Zn(DPM)_2$ and $Co(DPM)_2$ and thus is the first example of a tetrahedral iron(II) complex in which the metal is bonded to four oxygens. The room-temperature magnetic susceptibility of 5.0 B.M. confirms the presence of a spin-free $3d^6$ electron configuration and suggests a ^5E (in T_d) ground state. Attempts to observe the expected $^5T_2 \leftarrow {}^5E$ absorbance, which is found near 4000 cm.$^{-1}$ in $[FeCl_4]^{-2}$ species,[10] in reflectance spectra[11] were unsuccessful due to the presence of ligand overtones in the region in which the band should be found. The high-energy spectral cut-off for reflectance on the powdered solid appears near 10,000 cm.$^{-1}$. This suggests the presence of a low-energy electron-transfer band.

Experimental

Bis(2,2,6,6-tetramethyl-3,5-heptanediono)iron(II).—Ferrous sulfate (~1 g.) is dissolved in water (~15 ml.) to which one drop of sulfuric acid has been added. (The addition of acid prevents the slow formation of iron(III).) An excess of DPM is added to methanol (~30 ml.) and the two solutions are mixed, after exhaustive deoxygenation. A dilute aqueous solution of sodium hydroxide is added and, if oxygen has been rigorously excluded at all stages, a bright yellow precipitate is formed. The complex is washed free from traces of iron(III) by *n*-hexane, in which the $Fe(DPM)_3$ is very soluble. The bright yellow solid, which chars and smokes instantly when exposed to air, is dried under vacuum at room temperature.

Anal. Calcd. for $C_{22}H_{38}O_4Fe$: C, 62.6; H, 9.1; mol. wt., 422. Found: C, 62.4; H, 8.9; mol. wt. (cryoscopically in benzene), 418–435.

The magnetic susceptibility was determined at room temperature using the standard Gouy technique[12]: $\chi_g^{\text{uncor}} = 25.5 \times 10^{-6}$ c.g.s. unit at 20°, $\mu_{\text{eff}}^{\text{cor}} = 5.0$ B.M.

The X-ray powder pattern of the complex, sealed in a glass capillary, was observed with a Debye–Scherrer camera. The spacings of the first seven lines observed were (in Å.): 9.43 (s), 6.15 (m), 5.49 (w), 5.30 (w), 4.79 (m), 4.62 (s), 3.97 (w). Assuming the tetragonal cell constants[9] for $Zn(DPM)_2$, a = 10.67 Å., c = 21.76 Å., the first nine lines are calculated to be (*hkl* value in parentheses): 9.57 (011), 6.20 (112), 6.00 (013, vw), 5.43 (004), 5.34 (200), 4.79 (202), 4.66 (211), 4.03 (015), 3.99 (123). The X-ray powder photographs for the zinc(II), cobalt(II), and iron(II) complexes are nearly identical by a visual inspection.

Acknowledgment.—J. P. F. acknowledges support by the National Science Foundation, GP-196, for this work.

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[9] F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).

[10] C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.*, **25**, 159 (1963).

[11] Reflectance spectra were observed with powdered specimens held in a special holder fabricated for use with the standard attachment for a DK-2 spectrophotometer.

[12] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 415.

Correspondence

Bond Angles in the Binuclear Molybdenum(VI) Complex Anion $[MoO_2(C_2O_4)(H_2O)]_2O^{-2}$

Sir:

The crystal structure of the compound $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ has recently been reported by Cotton, Morehouse, and Wood[1] (CMW). It was found that the various Mo–O bond lengths and O–Mo–O bond angles varied considerably, and CMW stated that all of these variations appeared to correlate very well with simple considerations of interatomic repulsions and Mo–O bond orders. The six oxygen ligands of each molybdenum atom are of four types, namely, terminal, bridge, oxalate, and water, with respective Mo–O bond lengths[2] of 1.692–1.698, 1.874, 2.096–2.185, and 2.330 Å., and the bond angles range from 73.5 to 106.5°. In a short discussion of the bond angles, CMW noted that "the largest O–Mo–O angle is between the two terminal Mo–O bonds, which are the shortest ones. Because of the shortness of these *cis* Mo–O bonds, O · · · O repulsion tends to be large and is at least partially mitigated by expansion of the interbond angle." They also pointed out that the next largest angles are those between the terminal bonds and the bridge bond, and that the smallest angles (except in the chelate) are those between the very long $Mo–OH_2$ bond and its four *cis* neighbors.

This apparent correlation of the bond angles with the lengths of the two associated bonds has led us to make additional considerations of this interesting structure. The O · · · O distances associated with each of the bond angles were calculated. The results are presented in Table I. It is seen that although there is a wide variation among the bond angles, the O · · · O distances are, with the exception of the constrained oxalate group, rather similar. They average to 2.78 Å., a value equal, within experimental error, to twice the van der Waals radius[3] of 2.80 Å. The r.m.s. error in this average is 0.05 Å., or only slightly larger than the standard error of about 0.03 Å. in O · · · O distances. It would thus appear that the bond angles at the molybdenum atoms in the complex are

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[1] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

[2] These bond lengths, which were calculated with the lattice constants and positional parameters given by CMW (except that x of O_6 was taken as −0.0360 instead of +0.0360), differ by up to 0.012 Å. from the values in their paper. See their note which follows.

[3] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.

TABLE I

ANGLE AND DISTANCE DATA

Angle	Bond types	Value	O···O distance, Å.
O_5–Mo–O_6	Terminal–terminal	106.5°	2.72
O_5–Mo–O_8	Terminal–bridge	103.9°	2.81
O_6–Mo–O_8	Terminal–bridge	101.1°	2.76
O_6–Mo–O_1	Terminal–oxalate	94.3°	2.79
O_5–Mo–O_1	Terminal–oxalate	90.2°	2.70
O_6–Mo–O_2	Terminal–oxalate	89.6°	2.75
O_8–Mo–O_2	Bridge–oxalate	87.1°	2.80
O_5–Mo–O_7	Terminal–water	85.5°	2.77
O_1–Mo–O_7	Oxalate–water	80.6°	2.87
O_8–Mo–O_7	Bridge–water	80.2°	2.73
O_2–Mo–O_7	Oxalate–water	77.6°	2.83
O_1–Mo–O_2	Oxalate–oxalate	73.5°	2.56

determined almost entirely by the nonbonded O · · · O contacts within it.[4]

This behavior is in sharp contrast to that observed in some group IV and V molecules, data[5] for which are presented in Table II. The expected bond angle here is of course 109° 28′, and it may be seen that the deviations from this value are small indeed.

TABLE II

BOND ANGLES AND NONBONDED DISTANCES

Molecule, MH_l-$(CH_3)_mX_n$	Angle, X–M–X	Distance, X···X, Å.	Shortening from van der Waals sum,[3] Å.
$CH_2(OCH_2)_2$	112°	2.35	−0.45
CH_2F_2	111.9°	2.25	−0.45
CHF_3	108.8°	2.17	−0.53
NF_3	104.1°	2.16	−0.54
$SiHF_3$	108.3°	2.54	−0.16
CH_2Cl_2	111.8°	2.94	−0.66
$CHCl_3$	110.4°	2.90	−0.70
CH_3NCl_2	108°	2.82	−0.78
SiH_2Cl_2	110.0°	3.31	−0.29
$SiHCl_3$	109.4°	3.30	−0.30
$GeHCl_3$	108.3°	3.43	−0.17
$CHBr_3$	110.8°	3.18	−0.72
$SiHBr_3$	110.5°	3.55	−0.35
CHI_3	113°	3.54	−0.76

The conclusion seems inescapable that the use of the hydrogen-like sp^3 eigenfunctions in discussing the molecular geometries in relatively light atoms, such as C, N, Si, and Ge, is valid, while the use of hydrogen-like d^2sp^3 eigenfunctions for many-electron atoms is not. We refrain from pointing out further implications of this result. Additional structural data are obviously desirable.

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(4) An alternate explanation that the nature of the ligands changes the Mo orbitals from all being equivalent d^2sp^3 to hybrids $d^xs^yp^z$ having the observed bond angles is not only repugnant to us but also violates the rule of parsimony.

(5) L. Sutton, Ed., "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

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Response to Donohue's Note on Bond Angles in $[MoO_2(C_2O_4)(H_2O)]_2O^{-2}$

Sir:

In the preceding note, Donohue[1] has discussed our suggestion[2] that the O–Mo–O angles in $K_2[MoO_2(C_2O_4)(H_2O)]_2O$ are strongly influenced by the repulsive forces between nonbonded oxygen atoms. His demonstration that the various O · · · O distances are all about equal to one another and to the sum of the van der Waals radii provides a very neat confirmation of our suggestion.

We agree in general with his additional observations. It might perhaps be added that for an atom like Mo, where there are nine valence shell orbitals (4d, 5s, 5p) and only six atoms to be bonded to it, it is probable that satisfactory hybrid orbitals can be constructed for a variety of ligand–Mo–ligand angles, so that, within limits, angles can be adjusted to minimize repulsions without any serious loss in metal–ligand bond strengths. For lighter atoms, with fewer orbitals available, there are more stringent limitations on the distortions which can be tolerated without undue weakening of bonds.

We may also emphasize here that the effects reported and discussed by us for $[MoO_2(C_2O_4)(H_2O)]_2O^{-2}$ have also been found in dienMoO_3,[3] $[Mo(S_2COC_2H_5)_2O]_2O$,[4] and, most recently, in $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 5H_2O$.[5] The consistency of the effects leaves scarcely any question that they are real and that they are explicable in the terms discussed by ourselves[2–5] and Donohue.[1]

Finally, we wish to thank Professor Donohue for pointing out that there are slight discrepancies (~0.01 Å. in bond distances and ~0.2° in bond angles) between those he calculates from our atomic position parameters and those we recorded. These slight differences, which have no bearing on any of the conclusions and are scarcely significant even in a statistical sense, arose in the following way. Table I of ref. 2 gives the final atomic positional parameters obtained using weighted data, whereas, through an oversight, Tables III and IV give molecular dimensions computed from the atomic positional parameters obtained from the last cycle of refinement using unweighted data. Also, as Donohue rightly supposed, the x/a coordinate of O_5 should be −0.0360. This is purely a typographical error; all our computations were done using the correct figure.

Acknowledgment.—We thank Professor Donohue for showing us his manuscript in advance of publication.

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(1) J. Donohue, *Inorg. Chem.*, **4**, 921 (1965).

(2) F. A. Cotton, S. M. Morehouse, and J. S. Wood, *ibid.*, **3**, 1603 (1964).

(3) F. A. Cotton and R. C. Elder, *ibid.*, **3**, 397 (1964).

(4) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

(5) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, in press.

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