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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