TABLE I

RESULTS OF GEOMETRY CALCULATIONS ON EIGHT-COORDINATE CHELATE COMPLEXES

Complex[a]	Required symmetry[b]	d_T, Å[c]	d_S, Å[d]	Angle, deg[e]	Reported CP[f]	Ref
$Y(hfa)_4^-$	2	0.07, 0.07	0.19, 0.19	88.3	D	7
$Pr(tta)_4^-$	. . .	0.06, 0.07	0.17, 0.16	86.8	D	8
$Zr(ox)_4^{4-}$	2	0.11, 0.12	0.20, 0.20	88.7	D	9
$Zr(acac)_4$	2	0.30, 0.31	0.03, 0.03	83.3	A	10
$Eu(tta)_3(H_2O)_2$	. . .	0.43, 0.28	0.00, 0.02	78.0	A	11
$Y(acac)_3(H_2O)_2$	. . .	0.14, 0.20	0.07, 0.21	86.1	A	12
Perfect antiprism	$\bar{4}2m$	0.37, 0.37[g]	0.0	77.4	A	. . .
Perfect dodecahedron	$\bar{8}2m$	0.0	0.31, 0.31[g]	90.0	D	. . .

[a] Ligand abbreviations: hfa, hexafluoroacetylacetonate; tta, thenoyltrifluoroacetonate; ox, oxalate; acac, acetylacetonate. [b] From space group symmetry. [c] d_T is the average distance of ligand atoms from best plane through two intersecting trapezoids of dodecahedron. [d] d_S is the average distance of ligand atoms from best plane through two square faces of antiprism. [e] Angle between two intersecting trapezoidal best planes. [f] A = square antiprism; D = dodecahedron; polyhedron chosen by the original authors to describe their results. [g] Assuming a metal–ligand bond distance of ~2.6 Å; it should be noted that the entries reported in the table will decrease with decreasing metal–ligand bond distances.

great as the deviations of the atoms from the best square planes, d_S. Even better results were obtained for the other three complexes mentioned above. Thus both the angle and the mean displacement of ligand atoms from the appropriate best planes lead to an unambiguous choice of CP for these four complexes.

For $Zr(acac)_4$, the angle is midway between the ideal values, demonstrating that whichever idealized polyhedron is adopted, it will have to be recognized as significantly distorted. The original authors chose to describe the complex as an antiprism and, from a comparison of d_T and d_S (Table I), their choice appears to have been a sensible one. Of interest is the authors' comment[10] that the deviations from their idealized choice of geometry (square antiprism) were such that the molecule tended toward dodecahedral symmetry. It appears to be generally true that the observed distortions of either polyhedron are toward the other.

In the case of $Y(acac)_3(H_2O)_2$, the angle of 86.1° clearly points to the dodecahedron as the most suitable CP, whereas no distinction seems possible on the basis of d_T and d_S values. Using the dodecahedral model, the three chelating ligands are found to span *m* edges with two water molecules occupying the remaining A and B sites (see ref 2 and Figure 2 for nomenclature adopted here). This ligand-wrapping pattern is quite reasonable, since bidentate chelates have been found to span dodecahedral *m* edges in a variety of other complexes.[1] The original authors, on the other hand, discuss their results using the square antiprism as the idealized CP.[12] In particular, they compare the observed average polyhedron-shape parameters with those calculated by Hoard and Silverton[2] for minimization of ligand repulsive energy and imply good agreement. We have made an analogous comparison for the dodecahedral model, the results of which are shown in Table II along with the treatment of the original authors. In some cases the values reported in the table obscure wide variations in the individual shape parameters being averaged. This occurs for both idealized models and is not unexpected for a mixed-ligand complex. It is evident, however, that since the agreement for the dodecahedron is about as good as that for the antiprism, no choice can be made on this basis.

TABLE II

AVERAGE POLYHEDRON-SHAPE PARAMETERS FOR $Y(acac)_3(H_2O)_2 \cdot H_2O$[a,b]

Dodecahedral model			Antiprismatic model		
Parameter	Complex	MFP[c]	Parameter	Complex	MFP[c]
a	1.22	1.17 (1.20)	*l*	1.27	1.26 (1.26)
m	1.17	1.17 (1.20)	*s*	1.20	1.19 (1.26)
g	1.22	1.24 (1.20)	*l/s*	1.06	1.06 (1.0)
b	1.47	1.49 (1.50)	θ, deg	57.1	57.3 (59.3)
θ_a, deg	37.1	35.2 (36.9)			
θ_b, deg	71.2	73.5 (69.5)			

[a] All parameters refer to those defined by Hoard and Silverton[2] and are normalized by the average Y–O bond length, 2.39 Å.[12] [b] Data for the complex taken from ref 12; average values only are reported. Intersecting dodecahedral trapezoids have been taken as O_1, O_9, O_3, O_6 and O_4, O_5, O_7, O_8 of the original reference. [c] Most favorable polyhedron, calculated to minimize ligand repulsive energies; numbers in parentheses refer to the hard-sphere model (HSM) values.[2]

In conclusion, we wish to emphasize that the criteria proposed here are intended as an aid to identifying a particular eight-coordinate complex with either idealized polyhedron. They are not meant to provide a means of assigning a CP to a complex which is clearly intermediate between the two configurations (Figure 1). For such cases it is not really important whether one describes the molecule as a distorted square antiprism or distorted dodecahedron, so long as the choice is recognized as ambiguous. Finally, it should be pointed out that the foregoing analysis could be applied to nontransition metal compounds of analogous geometry, *e.g.*, the polyhedral boranes. For such cases it would be sufficient to consider an arrangement of atoms in precisely the same manner as the eight ligand atoms in the above discussion for coordination compounds.

Acknowledgments.—We thank Dr. J. White for making structural information available to us prior to publication, Dr. S. J. LaPlaca for providing the stereodrawings, Mr. R. Grubbs for help with the calculations, and the National Science Foundation for financial support under grant GP-6758.

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Thermal Reactions in the Mass Spectrometry of Organometallic Compounds[1]

Sir:

Thermal reactions in the inlet system and/or the ion source of mass spectrometers cause data interpreta-

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2257.

tion problems and errors which are generally recognized by experienced mass spectrometrists. However, inexperienced investigators and casual readers of the literature too often ignore the problems or assume a negligible effect on mass spectral measurements. Unfortunately many workers, including the authors of this correspondence, hesitate to undertake definite tests of thermal effects because of the complex equipment[2-6] required to establish the exact nature of the thermal reactions and to identify positively the reactive intermediates and final products. Studies conducted here have demonstrated that simple adaptations of equipment common to modern mass spectrometers can be employed to indicate whether thermal reactions in the ion source are a potential cause of errors in mass spectral measurements. Results show that thermal effects can be particularly extensive for organometallic compounds. This conclusion is in agreement with the recently published results of Pignataro and Lossing[3] for a variety of metal carbonyls and derivatives. Since over 200 papers dealing with mass spectra and/or appearance potentials for organometallic compounds are in the recent literature, a plea for routine attention to this problem seems warranted. The tests for thermal reactions, as described here, using simple equipment are strongly recommended as a routine procedure to be employed whenever a lack of proper instrumentation[2,4] precludes completely definitive studies.[3-6]

A small electric furnace (Figure 1) can conveniently be placed around the vacuum line which connects the molecular leak to the mass spectrometer ion source. The reservoir (A) can be maintained at a low temperature suitable for sampling the material of interest and the furnace (C) can be rapidly cycled to temperatures up to 400°. Simple monitoring of the parent ion signal yields the temperature at which thermal reactions begin. The time-consuming operation of heating the entire inlet reservoir is eliminated, and the sample is preserved for additional measurements.

The straight-through furnace (C) approximates the wall collision conditions which exist in the ionization chamber. Actual flow conditions in an ionization chamber of conventional design are such that molecules average more than 20 wall collisions before being exhausted. Certainly fewer collisions than this occur on the hot-wall surface of furnace C. For this reason, the temperature established by this procedure is a definite upper limit to be employed for the ionization chamber.

As an example, the decomposition temperatures for the apparently stable hexacarbonyls of Cr, Mo, and W were established by this procedure. The onset temperatures for decomposition as shown in Figure 2 are all below the ion-source temperature employed for the mass spectral study of many organometallic compounds. The surface catalytic nature of these reactions is illustrated by comparing Figure 2 to Figure 3. The data in Figure 3 were obtained from a second furnace-heating cycle which immediately followed the first decompositions. In this case the $Cr(CO)_6$ and $Mo(CO)_6$ began to decompose at an appreciably lower temperature. Apparently, these metal carbonyls can generate catalysts by depositing active metals and/or free radicals on heated-wall surfaces inside the mass spectrometer as has been shown recently to occur in the decomposition of $Ni(CO)_4$.[5] For this reason, the authenticity of the mass spectra of these and similar samples is dependent not only upon the ion-chamber temperature but also on the condition of the surfaces. If the wall surfaces inside the ion chamber are "clean" and the sample does not generate rapidly a new surface which is catalytic, then a relatively high ion-chamber temperature can be employed. However, this situation is unrealistic for general mass spectrometry studies, and the safest procedure is to operate the ionization chamber at as low a temperature as possible.

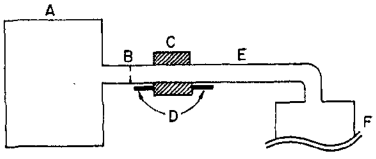

Figure 1.—Decomposition furnace used in conjunction with an all-glass molecular-leak heated inlet system: A, conventional molecular-leak reservoir; B, gold-foil pin hole; C, variable-temperature furnace; D, temperature sensors; E, 8-mm o.d. glass connecting tube; F, vacuum housing for the ion source of the mass spectrometer.

These results for the Cr, Mo, and W hexacarbonyls show that the ionization chamber temperature and cleanliness are the most important considerations in the mass spectrometry of metal carbonyls sampled from an external inlet system. When direct sample insertion is employed, the problem of thermal reactions in the ion chamber still exists. Most direct insertion devices do *not* generate a molecular beam and the gas flow inside the ion chamber is very similar to that which exists when an external system is employed. This is particularly true when the probe tip is more than a few millimeters away from the electron beam. Even when the probe tip is within 1–2 mm of the electron beam, only a slight reduction is achieved in the probability of thermal dissociation affecting the observed mass spectrum. In the absence of a condensation plate or a rapidly pumped "open" designed ion chamber, the sample molecules collide with the wall surfaces inside the chamber where possible decomposition products are formed. The probability for ionization of these products is almost as high as for the unreacted molecules.

We have used the direct insertion probe to study the thermal reactions of manganese and rhenium

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(2) R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 1523 (1962).

(3) S. Pignataro and F. P. Lossing, *J. Organometal. Chem.* (Amsterdam), **11**, 571 (1968).

(4) A. D. Norman, R. Schaeffer, A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 2151 (1966).

(5) S. M. Schildcrout, G. A. Pressley, Jr., and F. E. Stafford, *ibid.*, **89**, 1617 (1967).

(6) F. E. Stafford, G. A. Pressley, Jr., and A. B. Baylis, Symposium on the Applications of Mass Spectrometry in Inorganic Chemistry, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968.

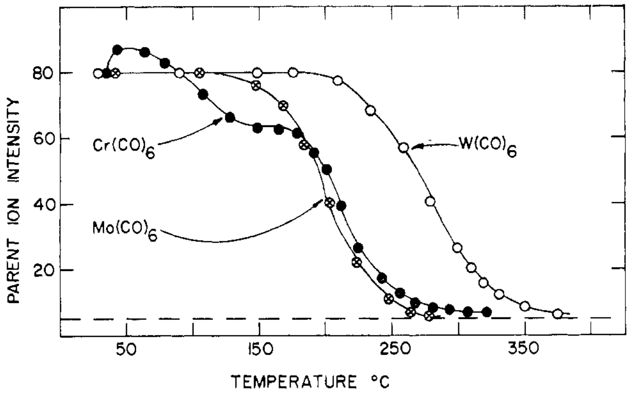

Figure 2.—Relative thermal stabilities of the hexacarbonyls of Cr, Mo, and W during the initial heating cycle of furnace C. Evidence that these carbonyls dissociate to the metal and CO was the observation of a rapid increase in the m/e 28 peak when the parent ion intensity began to decrease. A metallic mirror was also observed in the area of furnace C after repeated decompositions. Other reactive intermediates such as $M(CO)_y$ ($y = 1$–5) are neither confirmed nor ruled out by these results since the walls of tube E may selectively pump reactive intermediates.

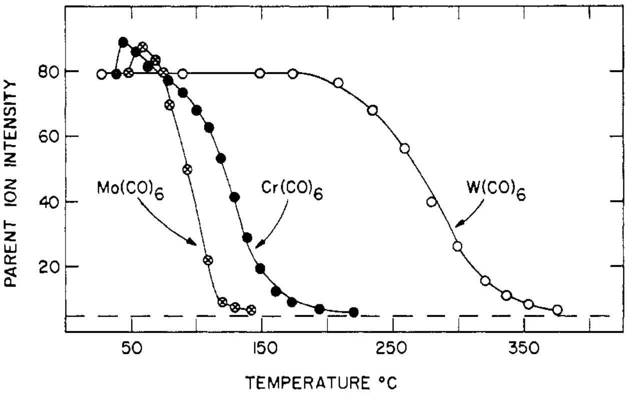

Figure 3.—Relative thermal stabilities of the hexacarbonyls of Cr, Mo, and W during the second heating cycle of furnace C.

pentacarbonyl halides. The results with $Mn(CO)_5Cl$ are given here since these are most illustrative. The more stable bromides and iodides react similarly but to a lesser extent.

The thermal reactions of these samples are complex and unexpected. On the basis of known solution chemistry and estimated bond energies[7] one might expect the thermal reactions

$$Mn(CO)_5Cl \longrightarrow \cdot Mn(CO)_4Cl + CO \qquad (1)$$

$$2(\cdot Mn(CO)_4Cl) \longrightarrow Mn_2(CO)_8Cl_2 \qquad (2)$$

to occur. Instead, the reactions

$$Mn(CO)_5Cl \longrightarrow \cdot Mn(CO)_5 + Cl \qquad (3)$$

and

$$2(\cdot Mn(CO)_5) \longrightarrow Mn_2(CO)_{10} \qquad (4)$$

are considered to take place on wall surfaces inside the mass spectrometer ion chamber. An external molecular leak (see Figure 1 reservoir (A)) was first used to introduce an authentic sample of $Mn(CO)_5Cl$ into the ion chamber (at 30–50°) of the mass spectrometer. The mass spectrum obtained with the reservoir at 80°, the furnace (C) at room temperature, and the ion chamber at 50° suggested that a considerable $Mn_2(CO)_{10}$ impurity was present. A repeat mass spectrum after 1 hr revealed that almost the entire sample was $Mn_2(CO)_{10}$. Obviously a thermal reaction had occurred in the sample reservoir (A). To check the nature of this reaction, tests were made using a cooled direction insertion probe[8] and the ion chamber at 30–50°. Under these sampling conditions an authentic mass spectrum of $Mn(CO)_5Cl$ was recorded and no peaks characteristic of $Mn_2(CO)_{10}$ were observed. When the ion chamber was heated above 50°, small peaks due to $Mn_2(CO)_{10}$ began to appear. To confirm the proposed thermal reactions, (3) and (4), the appearance potential of the $Mn(CO)_5^+$ ion was measured at various temperatures of the ion chamber. Significant measurements were made at ion-chamber temperatures of ~80 and ~100°. The measured appearance potentials using the vanishing-current procedure were 11.4 eV at 20°, 8.2 eV at 80°, and 9.4 eV at 100°. At room temperature the predominant electron-impact reaction was

$$Mn(CO)_5Cl + e^- \longrightarrow Mn(CO)_5^+ + Cl + 2e^- \qquad (5)$$

At 80°, the thermal reaction 3 occurs extensively and the electron-impact reaction is primarily

$$\cdot Mn(CO)_5 + e^- \longrightarrow Mn(CO)_5^+ + 2e^- \qquad (6)$$

At 110°, the $\cdot Mn(CO)_5$ radicals have combined to form $Mn_2(CO)_{10}$ by reaction 4 and the dominant electron-impact process is

$$Mn_2(CO)_{10} + e^- \longrightarrow Mn(CO)_5^+ + \cdot Mn(CO)_5 + 2e^- \qquad (7)$$

The measured value of 8.2 eV for reaction 6 compares favorably with 8.4 eV reported by Bidinosti and McIntyre.[9] This agreement supports the thermal dissociation interpretation. Support for reaction 7 is obtained by the excellent agreement of the 9.4-eV appearance potential with the appearance potential of $Mn(CO)_5^+$ from authentic samples of $Mn_2(CO)_{10}$.[9,10] Thus a range between 8.2 and 11.4 eV has been observed for the appearance potential of the $Mn(CO)_5^+$ ion from a sample of $Mn(CO)_5Cl$. The fluctuation in the measurement is caused by thermal reactions 3 and 4 which provide two additional sources for the $Mn(CO)_5^+$ ion. Similar effects may be responsible for discrepancies in the measured appearance potentials of fragment ions from other samples as has already been suggested.[11,12]

In conclusion, some precautions are worth stressing. (1) The catalytic effect can be operative even when all-glass systems are employed since coatings of active metals or low-volatility radicals may form rapidly.

(2) A temperature study with an externally heated

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[7] G. A. Junk, H. J. Svec and R. J. Angelici, *J. Am. Chem. Soc.*, in press.

[8] W. F. Haddon, E. M. Chait, and F. W. McLafferty, *Anal. Chem.*, **38**, 1968 (1967).

[9] D. R. Bidinosti and N. S. McIntyre, *Chem. Commun.*, 555 (1966).

[10] H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.*, **89**, 2836 (1967); see Table III.

[11] D. R. Bidinosti and M. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

[12] G. A. Junk and H. J. Svec, *Z. Naturforsch.*, **23b**, 1 (1968).

inlet system can be very deceptive if the temperature range is below the ion-chamber temperature.

(3) Reactions which occur in the mass spectrometer may be more pronounced than expected from other experimental evidence. For example, $Mn(CO)_5Cl$ can be purified by vacuum sublimation in a clean apparatus at 60° where gross amounts are transferred onto a cold glass surface. Yet this material will decompose in a few minutes after introduction into a previously used molecular-leak reservoir heated to only 50°.

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Transition Metal Nuclear Quadrupole Resonance. II. Interpretation of the Rhenium Nuclear Quadrupole Resonance Spectra in Dirhenium Decacarbonyl

Sir:

Since nuclear quadrupole resonance spectroscopy provides a sensitive measure of the charge and electron distribution in molecules, Re^{185} and Re^{187} nqr may be useful in the study of rhenium–rhenium[1,2] and rhenium–ligand bonds.

Although quadrupole coupling has been observed in the microwave spectrum of rhenium compounds,[3] to the author's knowledge the only pure Re^{185} and Re^{187} nqr have been detected[4] in dirhenium decacarbonyl. Because of the unusual nature of the results, no explanation has heretofore been proposed. This communication reports the low-temperature rhenium quadrupole coupling constant and offers a credible explanation for the anomalies.

All resonances (*cf.* Table I) were obtained on a high-power superregenerative spectrometer[5] and all frequency measurements were made utilizing spectrum-analyzing techniques.[6]

The rhenium field gradient, q_{zz}, and the asymmetry parameter, η, defined in terms of its irreducible tensor

$$\eta = (q_{xx} - q_{yy})/q_{zz}$$

components[7] can be calculated using solutions[8] of the secular equation for a nucleus with a spin of $^5/_2$ and the value for the electric quadrupole moment of Re^{187}.[9] The room-temperature values are $q_{zz} = -6.9 \times 10^{14}$ esu/cm^3 and $\eta = 0.63 \pm 0.03$ while the liquid nitrogen temperature values are $q_{zz} = -7.1 \times 10^{14}$ esu/cm^3 and $\eta = 0.88 \pm 0.03$. These results show that the "average"[10] field gradient tensor in the y direction is twice as large as the "average" field gradient tensor in the x direction at room temperature. This is totally unexpected in view of the symmetry[11] of $Re_2(CO)_{10}$. The D_{4d} "ideal" molecular symmetry requires C_{4v} site symmetry at the Re nucleus. Under a fourfold rotation axis q_{xx} should be the same as q_{yy}, *i.e.*, $\eta = 0$.

TABLE I

RHENIUM NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES

Nucleus	Transition	Temp, °C	Signal to noise ratio	Freq (±0.05), MHz
Re^{185}	$\pm^1/_2 \rightarrow \pm^3/_2$	26.5	11:1	28.94
Re^{187}	$\pm^1/_2 \rightarrow \pm^3/_2$	26.5	24:1	27.35
Re^{185}	$\pm^3/_2 \rightarrow \pm^5/_2$	26.5	44:1	39.93
Re^{187}	$\pm^3/_2 \rightarrow \pm^5/_2$	26.5	92:1	37.70
Re^{185}	$\pm^1/_2 \rightarrow \pm^3/_2$	−196	~10:1	35.67
Re^{187}	$\pm^1/_2 \rightarrow \pm^3/_2$	−196	~20:1	33.75
Re^{185}	$\pm^3/_2 \rightarrow \pm^5/_2$	−196	~30:1	39.80
Re^{187}	$\pm^3/_2 \rightarrow \pm^5/_2$	−196	~60:1	37.51

The deviations from ideal C_{4v} site symmetry in $Mn_2(CO)_{10}$[12] and $Tc_2(CO)_{10}$[13] are very small. In fact, all the measured bond angles and bond distances in both molecules are within three standard deviations of ideal D_{4d} molecular symmetry.

Unfortunately, precise structural parameters for $Re_2(CO)_{10}$ are not available from a two-dimension crystal structure.[11] However, it is difficult to imagine the $Re_2(CO)_{10}$ structure deviating enough from its $Tc_2(CO)_{10}$ and $Mn_2(CO)_{10}$ isomorphs to produce such a large asymmetry parameter.

Since the molecules are neutral, there can be no point charge lattice sum contributions to the field gradient in any direction. Induced dipole–induced dipole interactions cannot contribute any appreciable field gradient at the Re nucleus. At a distance of ~2 Å the induced-dipole interactions are about one-tenth the coulombic contributions and thus would account[14] for less than 1% of the total field gradient in neutral molecules.

There does appear to be a credible explanation for the large asymmetry parameter if one accepts structural isomorphism and assumes that the anisotropic temperature factors, B_{ij}, of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ are similar for $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$.[15]

It is interesting to note that in both $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ an analysis of the anisotropic temperature

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(1) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(2) F. A. Cotton, *ibid.*, **4**, 334 (1965).

(3) J. F. Lotspeich, *J. Chem. Phys.*, **31**, 633, 643 (1959).

(4) S. L. Segel and R. G. Barnes, *Phys. Rev.*, **107**, 638 (1957).

(5) C. B. Harris, unpublished work; G. E. Peterson, private communication.

(6) G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instr.*, **37**, 1081 (1966).

(7) T. P. Das and E. L. Hahn, *Solid State Phys. Suppl*, **1**, 4 (1958).

(8) M. H. Cohen, *Phys. Rev.*, **96**, 1278 (1954).

(9) H. Schüler and H. Korsching, *Z. Physik*, **105**, 168 (1937)

(10) The phrase "average" field gradient connotes the field gradient from contributions of electron distributions averaged over the dynamical properties of the solid, *e.g.*, large thermal or molecular vibrations in the lattice. The term molecular field gradient denotes the idealized field gradient of a nucleus at its zero-point vibrational energy.

(11) L. F. Dahl, I. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

(12) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(13) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).

(14) T. P. Das and E. L. Hahn, *Solid State Phys. Suppl.*, **1**, 165 (1958).

(15) $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ but not $Re_2(CO)_{10}$ crystal structures were refined anisotropically. The anisotropic temperature factors of both $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ indicate the same relative amplitude of anisotropic thermal motion in the same directions. It seems safe to assume that $Re_2(CO)_{10}$ should be similar to isomorphs in this respect.