factors shows significant differences in thermal motion of the carbonyls *cis* to each other. In $Mn_2(CO)_{10}$, for instance, the root-mean-square component of the thermal displacement lowers the Mn C_{4v} site symmetry to C_{2v}; *e.g.*, the CO's in the x direction have 30% less thermal displacement than the CO's in the y direction. Assuming a similar behavior in $Re_2(CO)_{10}$, the over-all effect, therefore, of the large anisotropic vibration is to leave q_{zz} relatively unchanged in both direction (along the Re–Re bond) and magnitude but to make $|q_{yy}/q_{xx}|$ much larger than 1. In other words, the "average" electron density around the Re is distributed more by thermal motion along the y direction than the x direction; thus, a large asymmetry parameter may be observed.

The increase in the low temperature η may be due to a decrease in the x and y motion but a greater decrease in the x direction. Low-temperature $Re_2(CO)_{10}$ anisotropic thermal parameters are needed to verify this point.

The room-temperature η can be estimated theoretically as follows. Consider the vibration of a carbonyl attached to a rhenium as depicted in Figure 1. Under the harmonic oscillator approximation the rms component of vibration along the M–CO bond can be calculated[16] from the anisotropic temperature tensors. In the case of $Mn_2(CO)_{10}$ there is a 30% difference between CO's *cis* to each other. Relating the rms amplitude to the exponentional function, σ, in a Gaussiun distribution, *i.e.*, rms amplitude $= (1/2\sigma)^{1/2}$ the expectation value of r^{-3} centered at the metal nucleus can be calculated, *i.e.*

$$\langle r^{-3} \rangle = (\sigma/\pi)^{1/2} \int_{-\infty}^{+\infty} r^{-3} e^{-\sigma(r-R_0)^2} \, \mathrm{d}r \tag{1}$$

where R_0 is the distance from the metal to the carbon. Using rms values for CO's in the x and y directions, respectively, as 0.26 and 0.18 Å, the expectation values of r^{-3} are calculated with $R_0 = 1.83$ Å as 0.157 and 0.161 Å^{-3}. Because the 5d radial wave functions of Re are so diffuse[17] (*cf.* Figure 2), the effect of a carbonyl vibration is transmitted the Re nucleus as a dynamical variation in the $\langle r^{-3} \rangle$ of the d electrons. One must consider the two electrons forming the Re–C σ bond as well as the four electrons participating in the Re–C π bond. These are depicted in Figure 2. Note that the π electrons are localized in a region of space about 45° off the Re–C bond. Because of the angular dependence in the field gradient tensor, the effects of all π electrons are about equal to those of the σ electrons. Thus eq 2 can be written, where N is the number of effective

$$\eta = \frac{(q_{xx} - q_{yy})_{\text{dynamical}} N (1 - \gamma_\infty)}{q_{zz}} \tag{2}$$

electrons projected on the Re–C bond and $(1 - \gamma_\infty)$ is the Sternheimer factor[18] for inner-core polarizations. The dynamical q_{xx} and q_{yy} are calculated as

(16) R. W. James, "The Optical Principles of the Diffraction of X-rays," G. Bell and Sons Ltd., London, 1962.

(17) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall Inc., Englewood Cliffs, N. J., 1963.
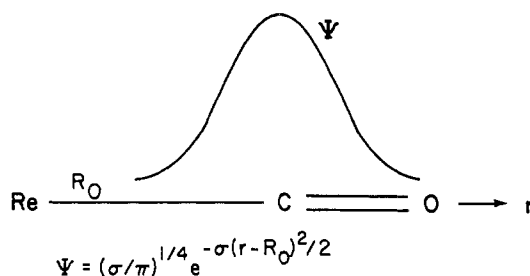

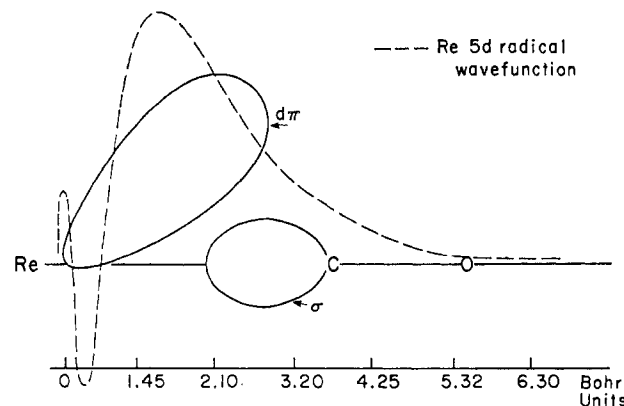Figure 1.—Coordinate system for $\langle r^{-3} \rangle$ and its relation to the CO vibrational amplitude.

Figure 2.—Radial 5d wave function for Re and its relation to the σ and π electrons in an Re–CO bond.

0.753×10^{14} and 0.772×10^{14} esu/cm^3, respectively, using the calculated $\langle r^{-3} \rangle_{x,y}$. N is equal to 4 and a $(1 - \gamma_\infty)$ of 28 is used[19] to calculate an η equal to 0.31. This compares favorably to the observed η of 0.63. It should be emphasized that the above is only a qualitative argument meant to show that dynamical vibration anisotropy can in a credible fashion account for a sizable η.

(18) R. M. Sternheimer, *Phys. Rev.*, **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954); **130**, 1423 (1963).

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

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Mössbauer Experiments on Iron(II) Phthalocyanine

Sir:

We wish to report the results of Mössbauer spectroscopic experiments on iron(II) phthalocyanines. Our independent experiments are very similar to those of

Hudson and Whitfield,[1] except that we have carried the experiments to lower temperatures and worked with different conditions in some cases. By studying the spectrum at 295, 77, and 4.6°K we have put an upper limit of 3.2 cm^{-1} for the splitting of any excited electronic state postulated to explain the intermediate susceptibility[2] of iron(II) phthalocyanine. This very low limit makes it quite likely that iron(II) phthalocyanine is a true "midspin" ($S = 1$) complex. We also observed the extraordinarily wide quadrupole splitting of bis(pyridine)iron(II) phthalocyanine, but we offer an alternative interpretation of this splitting to that offered by Hudson and Whitfield. Our new data are given in Table I, along with a comparison with the data of Hudson and Whitfield.

TABLE I

MÖSSBAUER DATA ON IRON(II) PHTHALOCYANINES

Temp, °K	Quadrupole splitting, mm/sec (±0.02)		Isomer shift, mm/sec (±0.02)	
	Moss and Robinson	Hudson and Whitfield	Moss and Robinson	Hudson and Whitfield
Iron(II) Phthalocyanine				
295	2.60	2.67	0.72	0.68
77	2.62	2.71	0.79	0.77
4.6	2.61	...	0.81	...
Bis(pyridine)iron(II) Phthalocyanine				
295	2.07	2.05	0.63	0.53
77[a]	1.96	1.89	0.62	0.62
77[b]	1.94	...	0.62	...
4.6	1.92	...	0.70	...

[a] Crystalline. [b] In frozen pyridine solution.

To form bis(pyridine)iron(II) phthalocyanine, 10 mg of Fe^{57} or Fe$^{57}_2$O$_3$ and 100 mg of phthalonitrile were mixed and heated at 300° in a sealed glass vial in a sand bath for 20 hr. Then the vial and product were pulverized and placed in a Soxhlet extractor. The product was washed in the extractor overnight with acetone, extracted with 20 ml of pyridine, and allowed to stand at 0°. Purple needle crystals, about 0.1 mm long, of bis(pyridine)iron(II) phthalocyanine formed slowly.

To form iron(II) phthalocyanine, the crude reaction product or the purified bis(pyridine)iron(II) phthalocyanine was sublimed in a quartz tube under oil pump vacuum at 400–425°. This produced purple needle crystals of iron(II) phthalocyanine. The iron(II) phthalocyanine could be converted into the bis(pyridine)iron(II) phthalocyanine by standing in pyridine.

The Mössbauer spectrometer has been described previously.[3] The isomeric shifts in Table I are relative to the center of a sodium nitroprusside doublet. Our own data, originally compared to the center of the Fe metal spectrum taken on our own spectrometer, were converted to the sodium nitroprusside standard of Hudson and Whitfield using the data of Fluck, et al.[4]

Hudson and Whitfield observed no temperature dependence of the quadrupole splitting of iron(II) phthalo-

(1) A. Hudson and H. J. Whitfield, *Inorg. Chem.*, **6**, 1120 (1967).

(2) A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

(3) A. J. Bearden, M. G. Hauser, and P. L. Mattern in "Mössbauer Effect Methodology," I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1965.

(4) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem.*, **2**, 277 (1963).

cyanine between 295 and 77°K. From this it can be inferred that for the abnormally high magnetic susceptibility value[2] (3.49 BM at 294°K) to be explained by a Boltzmann thermal mixture of a low-lying $S = 2$ state and a ground ($S = 1$ or $S = 0$) state, the $S = 2$ state would have to be within 54 cm^{-1} of the ground state. By working at 4.6°K, we have lowered this upper limit for the possible splitting. At 4.6°K, any low-lying excited state would have to be split by less than 3.2 cm^{-1} to be less than half occupied in a Boltzmann temperature distribution. Half-occupation of an excited state would have been clearly detectable in our Mössbauer experiments as either an additional pair of quadrupole lines or a change in the splitting of the single pair. Neither phenomenon was observed (Table I). This low limit for the splitting indicates that iron(II) phthalocyanine is probably a true case of an intermediate spin state. The explanation for the fact that its susceptibility is high even for an $S = 1$ state (spin-only moment = 2.84 BM at 294°K) should be sought in a large orbital contribution to its magnetic moment, instead of a mixture of spin states.

In experiments on bis(pyridine)iron(II) phthalocyanine we observed (Table I) the same wide quadrupole splitting and unusual temperature dependence reported by Hudson and Whitfield. However, their suggested explanation for the temperature dependence, that lattice contraction may change the π-bonding characteristics of the complex with temperature, is not supported by our finding (Table I) that a frozen pyridine solution of the bis(pyridine)iron(II) phthalocyanine has the same quadrupole splitting at 77°K as the crystalline form at 77°K. The observed temperature dependence of the splitting may instead reflect only intramolecular changes with temperature.

To account for the large magnitude of the quadrupole splitting, Hudson and Whitfield suggest that there is a strong interaction of the nonaxially symmetric pyridine ligands with the iron d_{xz} and d_{yz} orbitals. Their suggestion is supported by the observation that the low-spin complexes of *R. rubrum* and *Chromatium* cytochromes cc' or *Chromatium* cytochrome c_{552} with axially symmetric CO ligands have quadrupole splittings of only about 0.3 mm/sec.[5] However, the quadrupole splittings of bis(pyridine)mesoheme and bis(pyridine)diacetyldeuteroheme are 0.76 and 1.17 mm/sec, respectively.[6] These values are much lower than those observed for bis(pyridine)iron(II) phthalocyanine, even though these molecules are also not axially symmetric. Moreover, these results show that the quadrupole splitting can vary substantially with the electronegativity of the ring substituents. The wider quadrupole splitting of the diacetyldeuteroheme has been interpreted in terms of the greater electron-withdrawing power of the acetyl group relative to the ethyl group of the mesoheme.[1] Delocalizing electronic charge from the pyrrole nitrogens in the acetyl compound

(5) T. H. Moss, A. J. Bearden, R. G. Bartsch, and M. A. Cusanovich, *Biochemistry*, **7**, 1583 (1968).

(6) A. J. Bearden, T. H. Moss, W. S. Caughey, and C. A. Beaudreau, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1246 (1965).

would increase the asymmetry between the pyrrole and pyridine nitrogens and thus increase the quadrupole splitting. The very extensive π system of the phthalocyanine ring allows for even greater delocalization of electrons from pyrrole nitrogen π orbitals, and it may be that it is this characteristic of the molecule, rather than the axial asymmetry of the pyridine ligands, which causes the large quadrupole splitting. Mössbauer experiments on iron(II) phthalocyanine with axially symmetric ligands (like CO) would show which of these two explanations for the large quadrupole splitting is correct.

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Monodentate Ethylenediamine Complexes of Chromium(III)

Sir:

A recent paper by Childers, *et al.*,[1] reported the successful chromatographic isolation of the pentaaquo(2-aminoethylammonium)chromium(III) cation, $Cr(enH)(OH_2)_5^{4+}$, supposedly the first isolation of a complex of chromium(III) with a monodentate ethylenediamine ligand. A chromium(III) complex containing monodentate ethylenediamine may have been prepared more than half a century ago by the founder of coordination chemistry, Alfred Werner.

In an unpublished, but complete, typewritten manuscript dated June 1916, Werner described the preparation, properties, and constitution of a series of chromium complexes which apparently still remains unreported in the published literature. He formulated the parent compound as $H[Cr(en)_2Cl_4]$ and postulated a coordination number of 8 for chromium in this compound in analogy with its heavier congeners molybdenum and tungsten. We have been unable to prepare these compounds according to Werner's directions, but, on the basis of preliminary reflection spectra of Werner's samples (courtesy of Anorganisch-Chemisches Institut der Universität Zürich), Jørgensen[2] has tentatively identified the chloride of the series as 1,2,3-[Cr(en)(enH)Cl₃]Cl, a compound of hexacoordinated chromium containing both bidentate and monodentate ethylenediamine.

Werner's original paper has recently been published both in English[3] and German.[4] Small samples of Werner's compounds are available from the author.

(1) R. F. Childers, K. G. Vander Zyl, D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749 (1968).
(2) C. K. Jørgensen in "Werner Centennial," G. B. Kauffman, Symposium Chairman, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, pp 163, 164.
(3) G. B. Kauffman, *Chymia*, **12**, 217, 221 (1967).
(4) G. B. Kauffman, *Naturwissenschaften*, **54**, 573 (1967).

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