and CCl_4 has been determined for initial OsO_4 concentrations of 10^{-3} to 10^{-4} M.[2,3] Polymerization of OsO_4 into tetramers in CCl_4 also has been reported,[4] but this conclusion has been criticized.[5] Because polymerization of OsO_4 would cause the partition ratio to be concentration dependent, a study of the distribution of OsO_4 as a function of concentration was made using osmium-191 tracer. The results show no concentration dependence over a wide range and are in agreement with the previously reported values for the partition ratio of OsO_4.

Experimental

Reagents.—A standard OsO_4 solution, 4.43×10^{-3} M, in 0.1 N H_2SO_4 was prepared by dissolving 0.5 g. of analytical reagent grade perosmic acid (Mallinckrodt No. 2768) in 500 ml. of 0.1 N H_2SO_4 and standardizing this solution by ultraviolet spectrophotometry.[6]

Osmium-191 tagged solutions were prepared by adding osmium-191 (available from Oak Ridge National Laboratory) to 10 ml. of standard osmium solutions. Initial experiments indicated that not all the active osmium was present as OsO_4, and, therefore, this solution was extracted five times with 10 ml. of analytical reagent grade CCl_4, a sufficient number of times to remove all the inactive OsO_4. The extracts then were diluted to a specific volume with CCl_4 to provide solutions of known OsO_4 concentration and containing tracer osmium as OsO_4. In one experiment no inactive osmium was added to the tracer. The radiochemical purity of these solutions was checked.

Extraction Procedure.—Portions of the tagged OsO_4 solutions in CCl_4 (10 ml.) were equilibrated with an equal volume of either distilled, de-ionized water or 1.0 N $NaClO_4$ by mechanical stirring for 10 min. Aliquots of both phases were withdrawn, placed in a 10 × 75 mm. Pyrex tube with a cork stopper, and immediately counted in a well-type γ-scintillation detector for a sufficient length of time so that the standard deviation was less than 1%. It was found that after several hours the osmium activity tended to accumulate in the cork. Material balances indicated no loss of osmium activity during the extraction.

Results and Discussion

Data for the distribution of OsO_4 at the tracer level and at other concentration levels are presented in Table I. The results show no dependence on the osmium concentration and are in agreement with previously reported values of 12.3[2] and 13.0[3] at zero ionic strength and 14.8[3] at 1.0 M ionic strength. Assuming that polymerization is negligible in 10^{-9} M OsO_4 solutions in CCl_4, it is apparent that any polymerization in more concentrated solutions also must be very small.

TABLE I

PARTITION RATIO OF OsO_4 AT VARIOUS CONCENTRATION LEVELS

Initial concn. of OsO_4 in CCl_4, M	D = (c.p.m./ml.) org./(c.p.m./ml.) aq. Ionic strength 0.0	1.0
$\sim 10^{-9}$	12.4	14.7
8.86×10^{-6}	11.9	14.4
8.86×10^{-5}	12.2	14.2
8.86×10^{-4}	12.1	15.0
Average	12.2	14.6

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Correspondence

π-Bonding in Transition Metal Complexes

Sir:

The two types of π-bonding in transition metal complexes commonly are referred to as ligand-to-metal and metal-to-ligand. In the first instance the more stable π-molecular orbital for an interacting metal–ligand π-orbital pair mainly is located on the ligand, and in the second instance the more stable π-molecular orbital mainly is located on the metal. For octahedral complexes, there are three metal d-orbitals of the π-type; thus it is possible to make a total of three pure π-bonds ($^1/_2$ for each ligand).

For distorted octahedral complexes, the principal problem is in describing how the three d_π-orbitals are distributed among the ligands. In recent papers, we have considered the electronic structures of metal complexes exhibiting extremes of ligand-to-metal (MO oxycations)[1-3] and metal-to-ligand (M–NO nitrosyls)[4,5] π-bonding In sorting out the π-bonding in these distorted octahedral complexes, we formulated the rule given below.

For distorted octahedral complexes with tetragonal symmetry (ML_5X), nearly all the π-bonding is axially directed and involves the metal d_{xz} and d_{yz} orbitals. The stronger axial π-bonding may be either M–X or M–L, depending on whether the π-orbital energies of X or L more closely approximate the metal d_π orbital energies. It is a good approximation to neglect planar π-bonding and approximate the metal d_{xy} orbital as non-bonding.

In the case of vanadyl complexes, the optical spectral,[1,6] e.s.r.,[1,6] and the infrared[7] evidence, as well as

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unusually short V–O bond distances,[1] overwhelmingly support such a view. However, there is some difference of opinion with regard to metal nitrosyls. Naiman[8] considered NO^+ and CN^- as "about the same" and proceeded to assign the visible spectrum of $Cr(CN)_5NO^{3-}$ on the basis of the energy level scheme expected for octahedral $Cr(CN)_6^{5-}$. We followed the rule and considered the M–NO bond the most important part of the over-all electronic structure in $M(CN)_5NO^{n-}$ complexes; this leads to an energy level scheme which bears no resemblance to an octahedral level scheme.

Our main evidence for the higher order of the M–NO bond was the unusually short M–(NO) bond distance in a number of metal nitrosyls,[4] and the e.s.r. g-factor[9] of nearly 2 for $Cr(CN)_5NO^{3-}$. Since the publication of our papers[4,5] and Naiman's paper,[8] the following important evidence supporting our view has been presented.

(1) The visible absorption spectra of $Cr(CN)_5NO^{3-}$ and $Cr(H_2O)_5NO^{2+}$ are virtually identical[10]; both complexes exhibit three bands with nearly the same energies and intensities. This indicates that the Cr–NO bond dominates the over-all electronic structure and determines the relative energies of the metal d-orbitals.

(2) Recent Mössbauer effect measurements show that while the field gradient is zero at the ^{57}Fe nucleus in the $Fe(CN)_6^{4-}$ complex, the field gradient at the nucleus in $Fe(CN)_5NO^{2-}$ is substantial and over two times that of any other diamagnetic $Fe(CN)_5X^{n-}$ complex.[11,12] This confirms the belief that the metal pentacyanonitrosyls have "heavy" M–NO π-bonds, and are not in any sense octahedral.

The desire of the best π-bonding ligand in a metal complex to have exclusive rights to two metal d_π-orbitals leads to the kinetic phenomenon known as the *trans*-effect.[13] This process may be visualized either in ML_5X distorted octahedral complexes or in ML_3X distorted square planar complexes.

In at least one vanadyl ($VO(acac)_2$) and several metal nitrosyl ($M(NO)((CH_3)_2NCS_2)_2$) complexes, this axial elimination (of a hypothetical ligand) already has taken place, leaving a square- or rectangular-based pyramidal molecule. In fact, the only known square pyramidal type metal complexes have this feature of strong axial π-bonding.

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Nitrile Derivatives of Chromium Group Metal Carbonyls. II

Sir:

We wish to report novel acrylonitrile (AN) complexes of tungsten carbonyl. We have prepared $(AN)W(CO)_5$ (I) in which it appears that the AN is bonded to the tungsten by means of the lone pair of electrons on the nitrogen. The complex $(AN)_3W(CO)_3$ (II), on the other hand, appears to have the normal mode of attachment[1–3] (by means of the C=C π-electrons) but to possess novel C_{2v} structure for a trisubstituted hexacarbonyl.

I is prepared in virtually quantitative yield by stirring $(CH_3CN)W(CO)_5$[4] (III) overnight in excess acrylonitrile, followed by vacuum evaporation of the displaced acetonitrile and the excess acrylonitrile. *Anal.* Calcd. for $(H_2C{=}CHCN)W(CO)_5$: C, 25.5; H, 0.8; N, 3.71. Found: C, 26.23, 26.41; H, 1.29, 1.16; N, 3.88, 3.90. II is prepared by stirring $(CH_3CN)_3W(CO)_3$[5] (IV) in excess acrylonitrile overnight and evaporating the displaced acetonitrile and excess acrylonitrile. This compound is not very stable, has a poor analysis, and has some puzzling properties. *Anal.* Calcd: C, 33.7; H, 2.12; N, 9.85. Found: C, 30.45, 30.36; H, 1.75, 1.95; N, 6.50, 6.62.

The amorphous red solid, II, obtained from evaporation of excess acrylonitrile readily dissolves in acetone but soon crystallizes out and cannot be redissolved in acetone. The crystalline material can, however, be dissolved in acrylonitrile and upon evaporation gives the original amorphous solid. No changes in the infrared spectra are noted during these operations. Although the analysis for II would rather suggest the compound $(AN)_2W(CO)_4$, the facts that it is prepared from $(CH_3CN)_3W(CO)_3$, gives $[(C_6H_5O)_3P]_3W(CO)_3$ on treatment with triphenylphosphite in refluxing acetone without evolution of CO, and that only 3 equivalents of CO are liberated on treatment with excess I_2 in methanol lead us to propose the above structure.

Infrared spectroscopic evidence serves to indicate the manner of attachment of AN to the metal atom. I shows C≡N stretching absorption at 2239.3 cm.$^{-1}$ shifted to higher frequency from that in the free ligand (2235.3 cm.$^{-1}$), and a weak unshifted C=C stretching absorption at 1602 cm.$^{-1}$. The shift to higher frequencies of the nitrile absorption is due to the predominance of a kinematic effect[6] caused by bonding of the nitrile group through the nitrogen atom (verified in complexes known to contain this manner of attachment such as III and $RC{\equiv}N\cdot BCl_3$).[7] II,

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