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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KEMISK LABORATORIUM IV C. J. BALLHAUSEN
H. C. ØRSTED INSTITUTET
COPENHAGEN, DENMARK
DEPARTMENT OF CHEMISTRY HARRY B. GRAY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

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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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however, has the normal nitrile band at 2222.5 cm.$^{-1}$,[8] and no absorption at the normal C=C position similar to the data found for previously reported AN complexes of Mo[1] and Ni[2] carbonyls, in which the ligand is believed to be bonded to the metal through the C=C group (verified by X-ray diffraction for (AN)-Fe(CO)$_4$[3]).

Proton resonance lends unequivocal support to the above assignment. I shows a pattern essentially identical with the 13-line ABC type spectrum of pure AN, but generally shifted downfield by 0.5 p.p.m. This is consistent with assignment of such protons to carbon atoms not directly bonded to the metal, as, for instance, in III, where the proton singlet is seen shifted downfield 0.6 p.p.m. from that in pure acetonitrile. On the other hand, II shows a greatly perturbed proton resonance pattern, with a new singlet appearing far upfield (4.7 p.p.m.) and another one downfield (1.1 p.p.m.) from the center of the usual AN pattern, where only a few lines are now observed.

I was found to give a Diels–Alder adduct in high yield with cyclopentadiene on stirring overnight in alcohol. This product was identical with that obtained from displacement of acetonitrile with 2,2,1-bicyclo-2-heptene-6-carbonitrile. The *exo* and *endo*-cyclic isomers could be separated by thin layer chromatography. *Anal.* Calcd. for $(C_8H_9N)W(CO)_5$: C, 35.23; H, 2.05; N, 3.18. Found: C, 34.26, 33.78; H, 2.08, 1.87; N, 3.05, 3.06. The infrared nitrile frequency has been shifted from 2242 cm.$^{-1}$ in the free ligand to 2265 and 2278 cm.$^{-1}$ in the complexes, suggesting attachment *via* the nitrogen of the nitrile group. Furthermore I was recovered unchanged after treatment with 1 mole of H_2SO_4 and *t*-butyl alcohol in glacial acetic acid for 2 hr. These conditions typically cause alkylation of free nitrile groups giving N-substituted amides.[9] The absence of this typical organic reaction suggests that the nitrile group is tied up.

It is interesting to note that II shows three infrared active CO stretching absorptions (1980, 1911, and 1842 cm.$^{-1}$),[10] suggesting a *trans* structure (C_{2v}) even though it was prepared from IV, which has two CO bands, expected of an all-*cis* structure (C_{3v}).[11] The olefin group is well known, however, to have a strong *trans* effect in substitution reactions of its complexes,[12] which would apparently be above that of the carbonyl group in this case. The isomerization then would be expected to occur either during or after the substitution of three AN groups, through the directing effects of the metal-bonded C=C group.

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RESEARCH DEPARTMENT D. P. TATE
STANDARD OIL COMPANY J. M. AUGL
CLEVELAND 28, OHIO A. BUSS

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[8] Nitrile stretching frequency for I was measured in *n*-hexane solution, and that of II in acetone solution. These bands measured in Nujol appear at 2252 and 2221 cm.$^{-1}$, respectively.

[9] H. Plaut and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

[10] Metal carbonyl bands for II were measured in acetone, the corresponding bands appear at 1979, 1901, and 1833 cm.$^{-1}$ in Nujol.

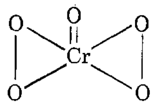
[11] R. Poilblanc and M. Bigorgne, *Compt. rend.*, **250**, 1064 (1960).

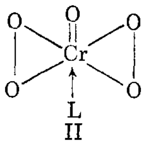
[12] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

The Structure of Perchromic Acid

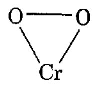
Sir:

We wish to comment on the structure (I) usually given for perchromic acid, CrO_5, and on the structures of some related compounds.


I

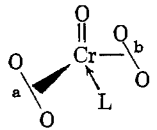

II

The first point is that I is inadequate in that this compound exists only in aqueous or non-aqueous (donor) solution, or as a solid formed with some donor molecule,[1] so that the structure always should be given as II, where L is H_2O, $(C_2H_5)_2O$, pyridine, phenanthroline, etc. The fact that the compound is highly reactive when L = H_2O does not affect this argument. Structure II contains formally six-coördinate Cr^{VI}, and although this probably is preferable to the five-coördination of I, it does not agree with the general finding that complexes of transition metals in very high oxidation states are tetrahedral. Further, and more important, both I and II require three-membered rings



with small O–Cr–O bond angles; the angle in K_3CrO_8, as found by X-ray methods,[2] is only 46°, implying considerable strain.

We believe that these difficulties can be avoided by regarding the O_2^{2-} groups as π-donors so that the Cr^{VI} is in fact tetrahedral (III), with the O_2^{2-} lying normal to the directions Cr–a and Cr–b. Donation from the filled π-orbitals of O_2^{2-} is analogous to that


III

suggested for olefin– or acetylene–transition metal complexes. Back-donation is impossible, both because of the formal absence of d-electrons on Cr^{VI}, and of the presence of filled antibonding orbitals in O_2^{2-}. However, the very high charge on the chromium should en-

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[2] R. Stomberg and C. Brosset, *Acta Chem. Scand.*, **14**, 441 (1960).