and a sample of $F_4Xe(OSO_2F)_2$ ($\sim$1 mmol) was decomposed after 2 weeks at 22° to the peroxide $S_2O_6F_2$ and XeF_4. Bis(O-fluorosulfato)difluoroxenon(IV) is more stable, but the decomposition is more complex, forming $S_2O_6F_2$, Xe, and XeF_4.

$$F_4Xe(OSO_2F)_2\ (0.90) \longrightarrow XeF_4\ (0.85) + S_2O_6F_2\ (0.94)$$

$$F_2Xe(OSO_2F)_2\ (1.0) \longrightarrow XeF_4\ (0.50) + Xe\ (0.45) + S_2O_6F_2\ (1.0)$$

This decomposition is similar to the Xe(II) fluorosulfates,[1,2] and the decomposition products were easily identified by their infrared spectra.[6–8] The decomposition of $F_4Xe(OSO_2F)_2$ provides a very convenient method for the formation of pure XeF_4, which is the most difficult of the xenon fluorides to obtain in high purity.[9,10]

The liquid compounds are extremely reactive and are comparable to XeF_6 in their reactivity. They react instantly with AgCl, forming a dark brown solid. The only suitable solvent we have found to date is $S_2O_6F_2$. The compounds are insoluble in *n*-perfluorohexane, slightly soluble with reaction in CCl_4, and react explosively with CH_3CN. They darken Kel-F No. 3 polymer oil but are unreactive toward polychlorofluoroethylene waxes and polyperfluoroether liquids. Their reaction with water is violent, and preliminary results indicate that the reactions parallel those of XeF_6 and XeF_4.

Caution! Both $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$ can form the highly explosive xenon trioxide with water and extreme care must be used in handling these compounds.

The ^{19}F nmr obtained in Kel-F tubes at 35° on a Varian A56-60 instrument showed the following adsorptions relative to external $CFCl_3$: $F_4Xe(OSO_2F)_2$, δ 129 (XeF) and 45 (SF); $F_2Xe(OSO_2F)_2$, δ 130 (XeF) and 46 (SF). The relative areas as shown by integration were 2.1:1.0 for $F_4Xe(OSO_2F)_2$ and 1.0:1.0 for $F_2Xe(OSO_2F)_2$. The observed chemical shifts for XeF show large changes compared to XeF_4 and XeF_6, while the SF resonance is very close to that of other covalent fluorosulfates.[11–13] The presence of small amounts of $S_2O_6F_2$ was evident by an adsorption at δ 44.8.[13,14]

The nmr resonances were broad at 35.0° with widths at half-height of about 3 Hz for SF and 25 Hz for XeF in both compounds. A variable-temperature study down to −70° resulted in further differential broadening of the lines with no resolvable coupling between the different fluorines. At −70° the samples were essentially solid. At −60° the XeF resonances were weak and broad and the SF absorptions were broadened to 26 and 9 Hz, respectively, for $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$. When the samples were run as 50% solutions in $S_2O_6F_2$ further line broadening was observed. The mechanism for the line broadening of the XeF and SF resonance is unclear and the question is under study.

The Raman spectra of the samples contained in ⅛-in. o.d. Kel-F tubes were taken on a Spex 4001 helium–neon laser instrument employing the 6328-Å line for excitation. The spectra recorded over the range of 300–1600 cm^{-1} show two very intense bands at 666 and 610 cm^{-1} for $F_4Xe(OSO_2F)_2$ and 670 and 614 cm^{-1} for $F_2Xe(OSO_2F)_2$. Xenon hexafluoride, $OXeF_4$, and XeF_4 show similar vibrational spectra.[8,15] These bands can be assigned to XeF stretching in the compounds. They are both shifted compared to the parent XeF_6 and XeF_4, with $F_2Xe(OSO_2F)_2$ showing the largest change. Several other weak bands similar to those observed for liquid $S_2O_6F_2$ run under the same conditions were also observed.

Attempts to obtain infrared spectra of the compounds have been frustrated by the high reactivity of the compounds and their low vapor pressure. No suitable ir solvent has been found and attempts to observe the gas-phase spectra at 35° are inconclusive.

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A Ruthenium Complex Having Both Linear and Bent Nitrosyl Groups

Sir:

The addition of small molecules to transition metal complexes and oxidative addition reactions in general have been extensively studied during the last 8 years,[1] with several very recent reports focusing on the oxidative addition properites of nitrosyl complexes of second and third transition series elements.[2–7] The recent communication of the synthesis of a ruthenium(0) nitrosyl analog[6] of the well-studied Ir(I) complex named after Vaska, $IrCl(CO)(P(C_6H_5)_3)_2$,[8] together with the established molecular geometry of the NO^+ adducts of $IrX(CO)(P(C_6H_5)_3)_2$ (X = Cl, I)[4,9,10] prompted us to consider the possibility of obtaining a complex having both linear and bent coordinated nitrosyl groups. We now wish to report the synthesis and structural

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elucidation of the NO+ adduct of $RuCl(NO)(P(C_6H_5)_3)_2$, which represents the first example of a complex exhibiting *both* types of nitrosyl coordination.

The complex $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]$ was synthesized in a manner similar to that used by Hodgson, *et al.*,[4] for the preparation of the analogous Ir complexes. A methanol solution of $NO^+PF_6^-$ was added under nitrogen to a green benzene solution of the neutral complex $RuCl(NO)(P(C_6H_5)_3)_2$, which had been prepared as described previously[6] by the zinc dust reduction of $RuCl_3(NO)(P(C_6H_5)_3)_2$. Most of the methanol was then drawn off using an aspirator pump and the remaining solution was allowed to stand for several days. Orange crystals of the desired complex separated out, and they were filtered and washed with cold benzene. *Anal.* Calcd for $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]\cdot C_6H_6$: C, 53.5; H, 3.8; N, 3.0; Cl, 3.8. Found: C, 53.7; H, 3.7; N, 2.8; Cl, 4.2. An infrared spectrum of the complex (KBr pellet) showed two bands at 1687 and 1845 cm^{-1} in the region assignable to coordinated ν(N–O). The band at 1687 cm^{-1} is in close agreement with the value of 1680 cm^{-1} observed for the $[IrCl(NO)(CO)(P(C_6H_5)_3)_2]^+$ complex.[4]

A parallelepiped-shaped crystal of approximate dimensions 0.13 × 0.14 × 0.20 mm suitable for single-crystal X-ray study was then mounted, and Weissenberg and precession photographs revealed the complex to crystallize in the monoclinic space group $P2_1/c$ in a cell of refined dimensions a = 12.51 (2) Å, b = 14.67 (2) Å, c = 23.00 (2) Å, β = 91.84 (2)°, and V = 4219 Å.[3] An experimental density of 1.49 (1) g/cm^3, obtained by the flotation method, agrees with a calculated value of 1.484 g/cm^3 for four formula weights corresponding to $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]\cdot C_6H_6$ per unit cell.

A complete set of independent intensity data within the angular range 5° < 2θ < 40° was collected by the θ–2θ scan technique using a Picker four-circle automated diffractometer. Zr-filtered Mo Kα radiation and pulse-height analysis were employed for the data collection. The intensities of a total of 4187 reflections were measured, of which 2293 reflections were observed to be greater than 1.5σ. The intensity data were corrected for Lorentz and polarization effects, but not for absorption, owing to the smallness of the linear absorption coefficient (μ = 6.1 cm^{-1}) and the approximate uniformity of crystal dimensions. The structure was solved by standard Patterson and Fourier methods, and refinement was carried out using a least-squares procedure. In the refinement, the atoms of the nitrosyl ligands as well as the ruthenium, chlorine, and cation phosphorus atoms were allowed to vibrate according to an anisotropic thermal model, while all other atoms were restricted to isotropic thermal motion. The phenyl rings were treated as rigid groups in the refinement. This refinement of positional and thermal parameters and a single scale factor converged to a conventional R factor of 0.075 and weighted R factor, R', of 0.075 for 2293 reflections above 1.5σ. A final difference Fourier based on this refinement together with the isotropic thermal parameters of the anion fluorine atoms suggested the possibility of disorder or significant anisotropic movement of the PF_6^- group in the crystal, and further refinements using different models for the PF_6^- group are under study.

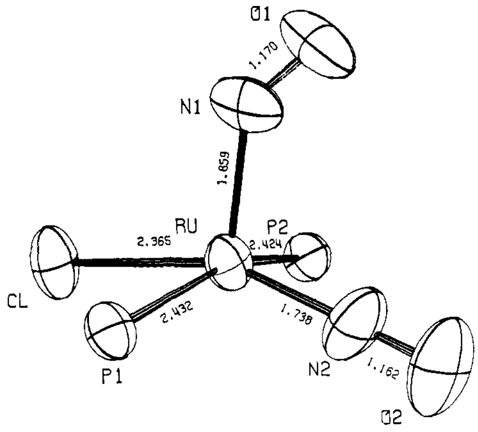

Figure 1. A perspective drawing of the inner coordination geometry of $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$. The estimated standard deviations for the bond lengths shown are: Ru–N, 0.016; Ru–P, 0.005; Ru–Cl, 0.005; N–O, 0.016 Å.

The structure of the Ru dinitrosyl cation is best described as that of a distorted tetragonal pyramid in which two trans phosphorous atoms, the chlorine atom, and one nitrosyl group comprise the base of the pyramid, while the other nitrosyl group forms the apex. A perspective view of the inner coordination geometry of the complex is presented in Figure 1 along with the important intramolecular distances. Important intramolecular angles are given in Table I. The most chemically interesting feature of the structure is the striking difference in the coordination of the two nitrosyl groups. The nitrosyl located in the base of the pyramid is bonded to the ruthenium in an essentially linear manner with a relatively short Ru–N distance of 1.74 (2) Å and a Ru–N–O bond angle of 179 (2)°, whereas the nitrosyl located at the apex coordinates in a bent manner with a longer Ru–N distance of 1.86 (2) Å and a Ru–N–O bond angle of 136 (2)°. The molecular geometry of $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$ is thus analogous to that observed for the isoelectronic NO+ adducts, $[IrCl(CO)(NO)(P(C_6H_5)_3)_2]^+$ and $[IrI(CO)(NO)(P(C_6H_5)_3)_2]^+$, in which the nitrosyl is located at the apex of the square pyramid with Ir–N–O bond angles of 124.1 (9) and 125 (3)°, respectively.[9,10] An examination of the bond angles in Table I indicates that the ruthenium lies above the basal plane of the tetragonal pyramid. In contrast to the analogous Ir systems, the four donor atoms of the plane do not deviate significantly from the best least-squares plane calculated through them, the largest deviation being 0.045 (16) Å for N(2). The Ru is displaced 0.39 Å from this plane, as opposed to a 0.23-Å displacement for Ir in the iodo complex.[10] The greater displacement in the present structure possibly reflects the greater nucleophilicity of Ru(0) *vs.* Ir(I) in the related d^8 systems.

Table I. Important Bond Angles (deg)

Ru-N(1)-O(1)	136.0 (16)	N(1)-Ru-P(2)	97.1 (5)
Ru-N(2)-O(2)	179.5 (18)	N(2)-Ru-Cl	155.8 (6)
P(1)-Ru-P(2)	159.6 (2)	N(2)-Ru-P(1)	92.2 (5)
N(1)-Ru-N(2)	102.5 (8)	N(2)-Ru-P(2)	91.6 (5)
N(1)-Ru-Cl	101.6 (6)	P(1)-Ru-Cl	83.8 (2)
N(1)-Ru-P(1)	101.6 (5)	P(2)-Ru-Cl	84.5 (2)

The structure of $RuCl(NO)_2(P(C_6H_5)_3)_2^+$ makes possible a detailed comparison of the bond parameters of linear and bent nitrosyls, where previously such a direct comparison was not possible. The longer Ru–N distance (1.86 Å) of the apical nitrosyl group coupled with its N–O bond length of 1.17 (2) Å lends considerable support to the notion of the bent nitrosyl group coordinating as a σ Lewis acid in complexes of nucleophilic metal ions.[4,9,10] On the other hand, the shorter Ru–N distance of the equatorial nitrosyl and its linear coordination indicate it to bond to Ru as a strong π acid. The Ru–N(2) bond length of 1.74 Å is directly comparable to the corresponding distance of 1.72 Å found in the six-coordinated complex, $Ru(NO)(S_2CN(C_2H_5)_2)_3$,[11] in which the nitrosyl coordination is essentially linear. It is clear from these results that the infrared bands at 1845 and 1687 cm^{-1} are assignable primarily to ν(N–O) of the linear and bent nitrosyl functions, respectively.

One additional feature of the inner coordination geometry which is interesting to note is that the oxygen of the bent nitrosyl group is oriented toward the equatorial NO function. A direct, although weak, interaction between one of the π^* orbitals of the equatorial nitrosyl and one of the oxygen lone pairs of the apical ligand is thus possible. A similar orientation of the apical nitrosyl ligand toward the equatorial carbonyl is found in each of the analogous Ir systems.

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Book Reviews

Transfer and Storage of Energy by Molecules. Volume 1. Electronic Energy. Edited by GEORGE M. BURNETT, Professor of Physical Chemistry, University of Aberdeen, and ALASTAIR M. NORTH, Professor of Physical Chemistry, University of Strathclyde, Glasgow. Wiley-Interscience, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. xv + 234 pp. 15 × 23.5 cm. $11.95.

The objective of "Transfer and Storage of Energy" is to "... delineate the scope and (to) set down the fundamentals of the subject of Molecular Energy Transfer." There are to be five volumes in total, each edited by G. M. Burnett and A. M. North, and each consisting of a few articles by experts in various fields related to molecular energy transfer processes. This first volume "Electronic Energy Transfer'" contains four articles: (1) "Electronic and Vibrational Transfer in Gas Phase Systems," by R. B. Cundall; (2) "Thermal Population of Excited Electronic States—Excitation and Emission in Shock Waves," by J. N. Bradley; (3) "Chemistry of Electronically Excited States of Organic Molecules," by A. Kearwell and F. Wilkinson; (4) "Energy Transfer in Radiation Chemistry," by M. Burton, K. Funabashi, R. Hentz, P. K. Ludwig, J. L. Magee, and A. Mozumder.

This review will take the form of comments upon the book considered as a single entity, and also some brief remarks about the individual articles.

Each article makes interesting reading, and each is carefully set down with numerous references. None of the articles could be considered definitive either within the scope of the series or within the titled areas, and perhaps this is one reason why the book as a whole does not manage to realize the objectives of the editors. Another reason is that perhaps the fundamentals of a subject such as the transfer and storage of electronic energy are defined insufficiently at this time. In any case the book lacks the coherence that may have made it a significantly new contribution to this field. Many of the areas that are discussed are developing sufficiently rapidly now that it is doubtful whether this volume will make a significant continuing contribution within the context of the stated aims.

Article (1) is an extremely well-written discussion of energy transfer in atomic and molecular gases. The field—from sodium to 1,2-benzperylene—is covered in 56 pages with 205 references, of which 75% are from 1965 or earlier. Article (2) is a quite succinct account of energy transfer between translational and electronic states and is concerned with a documentation of known shock excitation phenomena. Article (3) contains a selection of elementary spectroscopic principles leading to some excited state characteristics for aromatic hydrocarbons and their derivatives; there are some compilations of data that could prove useful, but the theoretical scope is very limited. Article (4) is a commendable effort to present the language and principles of high-energy radiation effects in liquids.

It is my recommendation that people in chemical physics plan to read these articles, although no unifying features or coherence of subject matter should be anticipated.

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