observed even for moderately thin samples (~1.2 mm/sec), is broader than would be expected for an ideally cubic compound and suggests a small departure from such an idealized geometry, presumably due to the steric requirements of the ligands.

A crystal structure study of the tetrakis(*N*,*N*-diethyldithiocarbamato)tin(IV) has been published by Harreld and Schlemper,[28] who found a distorted octahedral environment around the tin atom with two monodentate and two bidentate ligands evident from the metal–sulfur bond distances. The departure from regular O_h symmetry is significant in this molecule in which the S–Sn–S bond angle is 70.6° for the chelated ligand and 99.7° for the S–Sn–S angle between the chelated and monodentate ligands. Finally, it is interesting to note that the S–Sn–S bond angle involving the two monodentate ligands is 81.1°, thus placing these two groups nearly cis with respect to each other, rather than in the trans position which might have been expected. The Sn–S bond distance for the nonbonded sulfur atom is 3.9 Å (compared to a van der Waals contact of 3.7 Å) and hence the monodentate ligand cannot be considered as anisobidentate in this structure.

The line broadening observed in the Mössbauer spectra (*vide supra* and Table I) reflects this departure from cubic symmetry and suggests a similarity between the structure of the tetrakis(*N*,*N*-dimethyldithiocarbamato) compound and the structure studied by Harreld and Schlemper. From the isomer shift–electronegativity correlation[12] the mean ligand–sulfur electronegativity is seen to be about 8.75 on the Jaffe–Mulliken scale, intermediate between the electronegativity of bromide and chloride bonded to Sn(IV). Beyond observing the internal consistency of this value for a tin–sulfur bonding interaction little further information can be extracted with confidence from the present data.

IV. Summary

The present study has served to elucidate the structure and bonding in a series of organotin(IV) dithiocarbamates by the use of infrared, nmr, and Mössbauer spectroscopies. In dialkyltin(IV) bis(dithiocarbamate) complexes the ligand acts as an anisobidentate moiety, the two sulfur atoms interacting unequally with the central metal atom to give rise to significantly distorted octahedral configurations about the tin atom. Mössbauer studies over the temperature range 78–150°K have shown that in $(CH_3)_2Sn(dtc)_2$, the solid is composed of monomolecular units and no evidence for intermolecular bridging by the sulfur-containing ligand in the solid is noted in the data. The metal atom vibration is essentially isotropic in this molecule over the indicated temperature range. In the case of the tetrakis(dimethyldithiocarbamate and -diethyldithiocarbamate) complexes of Sn(IV), there is no resolvable quadrupole splitting extractable from the Mössbauer data—although there is a noticeable line broadening observed in the spectra—and thus the charge distribution about the metal atom must be nearly ideally cubic, arising from the distorted octahedral ligand configuration about the metal atom involving two isobidentate and two monodentate ligands bonded to the central atom as indicated by published diffraction data. The present study has also permitted the evaluation of group electronegativities for alkyl and aryl groups bonded to Sn(IV), as well as for the ethyldithiocarbamate ligand in a series of structurally related compounds.

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Single-Crystal Electronic Spectra of a $NiPI_3$ Chromophore

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Single-crystal polarized spectra of tetraphenylarsonium triiodo(triphenylphosphine)nickelate(II), $[(C_6H_5)_4As][NiI_3\{P(C_6H_5)_3\}]$, have been recorded between 380 and 77°K. The $NiPI_3$ chromophore has an approximate C_{3v} symmetry; however, the observed polarization properties cannot be accounted for by axial symmetry. The band intensities are found to be temperature dependent. This has been discussed on the basis of a temperature dependent population of levels arising from low symmetry and spin–orbit coupling effects on the ^3E ground level.

Introduction

The technique of single-crystal polarized electronic spectroscopy has developed as a useful tool in gaining specific information about the electronic structure of the metal complexes.[1,2] However only a few high-spin nickel(II) complexes have been investigated.[3–7] Among the pseudotetrahedral chromophores, only

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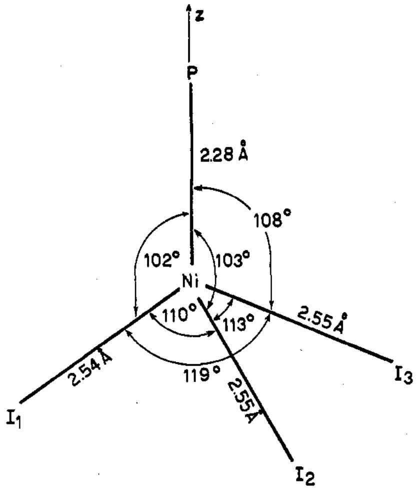

Figure 1.—Structure of the $NiPI_3$ chromophore.

the spectra of the $Ni\{(C_6H_5)_3P\}_2Cl_2$[8] and Ni(*N*-ethyl-1,4-diazabicyclo[2.2.2]octonium)X_3[9] complexes have been published, although the X-ray structure of the latter complex has not been reported.

We wish to report the single-crystal polarized electronic spectrum of tetraphenylarsonium triiodo(triphenylphosphine)nickelate(II), $[(C_6H_5)_4As][NiI_3\{P(C_6H_5)_3\}]$, in which the $NiPI_3$ chromophore has been shown by X-ray analysis to be pseudotetrahedral with an approximate C_3 symmetry axis.[10] For comparison purposes, the spectrum of the analogous $NiPBr_3$ chromophore[11] is also reported.

Experimental Section

Preparation of the Complexes.—The complexes $[(C_6H_5)_4As][NiX_3\{P(C_6H_5)_3\}]$, where X = Br and I, were prepared as previously described,[11] and single crystals suitable for spectroscopic measurements were obtained by slow evaporation of butan-1-ol solutions of the complexes at 70°. *Anal.* Calcd for $C_{42}H_{35}AsBr_3NiP$: C, 53.43; H, 3.74. Found: C, 53.74; H, 3.96. Calcd for $C_{42}H_{35}AsI_4NiP$: C, 46.49; H, 3.25. Found: C, 46.84; H, 3.42.

Crystallographic Morphology.—The dark red crystals of the iodide derivative are monoclinic[10] (space group $I2/c$), $a = 33.971$ Å, $b = 14.992$ Å, $c = 16.253$ Å, $\beta = 92.06°$, and $Z = 8$. The molecular structure is shown in Figure 1 along with bond distances, bond angles, and the molecular coordinate axes. The z axis has been chosen coincident with the pseudo-C_3 axis. The site symmetry of the nickel ion is C_1, however, the symmetry of the chromophore is not far from C_{3v}. The plate-like crystals obtained had the (100) face most highly developed, as confirmed by X-ray data. The spectra were recorded along the b and c axes. Along b the spectrum is expected 100% ⊥ polarized, whereas along c the polarizations are both ‖ (53%) and ⊥ (47%). Owing to the thinness of the crystals, attempts to record the spectra on a different face were unsuccessful.

Structural data are lacking for the bromide derivative. The green plate-like crystals were found not to be isomorphous with the iodide derivative. The spectra were measured along the extinction directions of the most developed face.

Physical Measurements.—Polarized spectra were measured using a Unicam SP-700 spectrophotometer modified with a homemade dewar to allow the recording of variable temperature spectra. The spectra were recorded at 380°K (using a water–glycol bath), at 300°K, at 195°K (with an acetone–Dry Ice bath), and at 77°K (liquid nitrogen temperature).

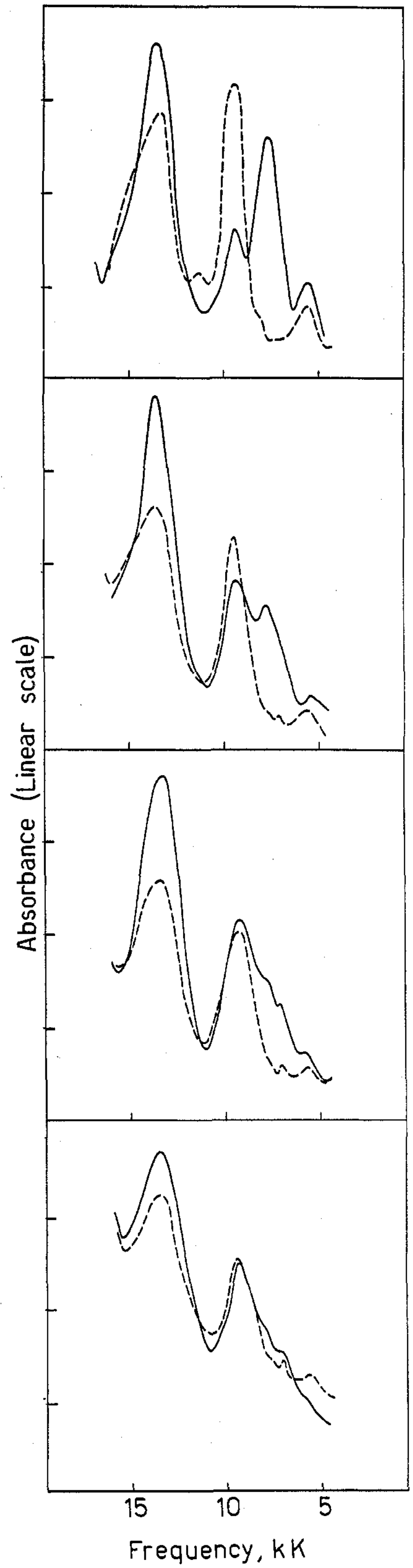

Figure 2.—Single-crystal polarized electronic spectra of the $NiPI_3$ chromophore recorded at (from the top) 77, 195, 300, and 380°K: —, ⊥; – – –, ‖ (53%) and ⊥ (47%).

Results

Single-crystal polarized electronic spectra of the $NiPI_3$ chromophore, recorded at 380, 300, 195, and 77°K, are shown in Figure 2 and those of the $NiPBr_3$ chromophore, recorded at 300 and 77°K, are shown in

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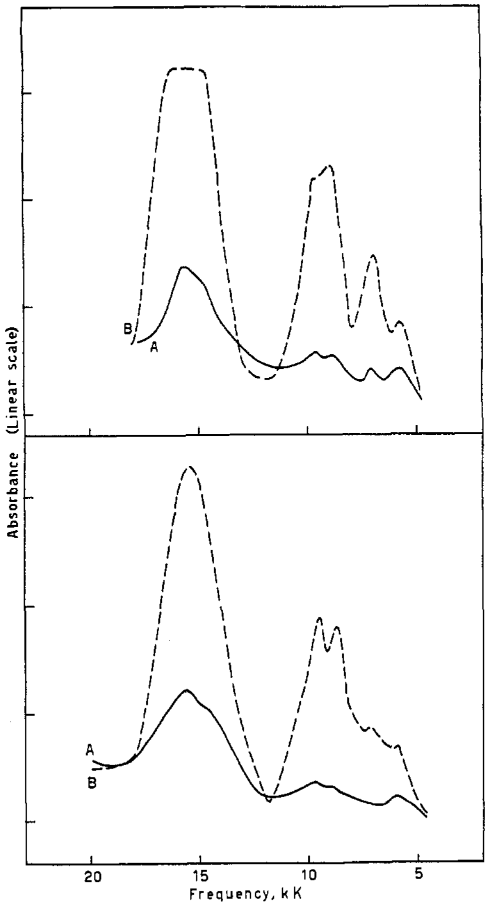

Figure 3.—Single-crystal polarized electronic spectra of the $NiPBr_3$ chromophore recorded at 77°K (top) and 300°K (bottom).

Figure 3. The spike at 7.1 kK, which is present in every spectrum, is attributed to the overtone of the O–H stretching of water vapor. Its appearance is due to improper balance of the light beams. The spectra of both complexes show a marked change in the polarization properties and relative intensities of the bands, whereas the frequency maxima remain substantially unchanged, apart from a hypsochromic shift of 0.2–0.3 kK as the temperature is varied from 380 to 77°K. In particular the spectra of the iodide complex recorded along the *b* direction show an increase of the peak at 7.8 kK and a decrease of the peak at 9.4 kK when the temperature is lowered. Also for the bromo derivative a change in the intensity of the bands at 8.8, 7.1, and 5.8 kK is observed although the spectrum along one extinction direction is always more intense. A marked sharpening of the bands also occurs with lowering temperature. The spectrum of $NiPI_3$ at liquid nitrogen temperature shows one more band at 11.3 kK whose intensity and frequency are strongly indicative of a spin-forbidden transition.

Discussion

The most interesting features of the spectra of the iodide and bromide derivatives are the drastic changes of the relative intensities and of the polarization properties of the bands with temperature. These changes are reversible and continuous and the number of the bands as well as their frequencies (within 0.3 kK) remain unaltered. In the range of temperatures investigated the single crystal does not show any apparent change of the morphology, and the extinction directions in polarized light remain unaltered. Therefore we conclude that the room temperature structural data of Figure 1 and the molecular orientation with respect to the crystallographic axes can be used as a basis for the discussion of the spectra.

The predominant mechanism under which the d–d transitions become allowed cannot be vibronic in nature owing to the high intensity of the bands (ϵ_M in solution varies from 200 to 800) and because this mechanism is expected to give rise to a decrease in intensity with temperature,[12] whereas intensity gains are actually observed. The transitions therefore must be allowed *via* a noncentric ligand field. However, the mixing of u states into the d levels *via* a static ligand field cannot alone explain the temperature dependent intensity of the bands since the extent of mixing does not depend on temperature.

Such effects of temperature on the band intensities could be accounted for by a population distribution over several levels close in energy to the ground level. Assuming a ligand field of C_{3v} symmetry to be operative and considering that the phosphorus donor atom exerts a stronger ligand field than Br^- and I^-,[13] the most stable configuration yielding a high-spin term must be (a_1e) corresponding to a ^3E ground level. Such a ground level is expected to experience a zero-field splitting owing to both low symmetry components of the ligand-field and spin–orbit coupling.[12] Low symmetry components may well originate from Jahn–Teller or static distortion. If the low symmetry matrix elements were small compared to kT, the spectra could be interpreted in terms of C_{3v} symmetry and the polarization properties would be those reported below

$$\begin{aligned} E \rightarrow E\ &(\parallel, \perp) \\ A_1\ &(\perp) \\ A_2\ &(\perp) \end{aligned}$$

Since the spectra of the iodide derivative recorded along *b* are expected to be ⊥ polarized and the spectra recorded along *c ca.* 0.5 || and 0.5 ⊥ polarized, the spectra can be interpreted in terms of axial symmetry only when the bands in the *c* direction are reduced at most to 50% of the intensity in the *b* direction. Therefore the spectra at temperatures lower than 380°K cannot be interpreted in terms of axial symmetry since the intensity of some bands (*e.g.*, that at 7.8 kK) decreases far more than 50%. The spectrum at 380°K might be interpreted on the analysis described above. In fact the bands at 13.4, 7.8, and 5.6 kK, whose intensity decreases to about 50% by passing from the *b* to the *c* direction, are ⊥ polarized whereas the band at 9.4 kK is polarized both || and ⊥. The assignment therefore would be the following: 13.4 kK, $^3E \rightarrow {}^3A_2(P)$; 9.4, $^3E \rightarrow {}^3E(P)$; 7.8, $^3E \rightarrow {}^3A_2$; and 5.6, $^3E \rightarrow {}^3A_1$. This assignment, however, is not consistent with the spectra of the $NiPBr_3$ chromophore. The latter complex shows two high-frequency bands at 15.0 and 9.8 kK which apparently correspond to the 13.4 and 9.4 kK bands of the iodide derivative. If these two bands were due to F → P transitions, one would expect higher frequencies for the bromo than for the iodo derivative owing to both the stronger ligand field of Br as com-

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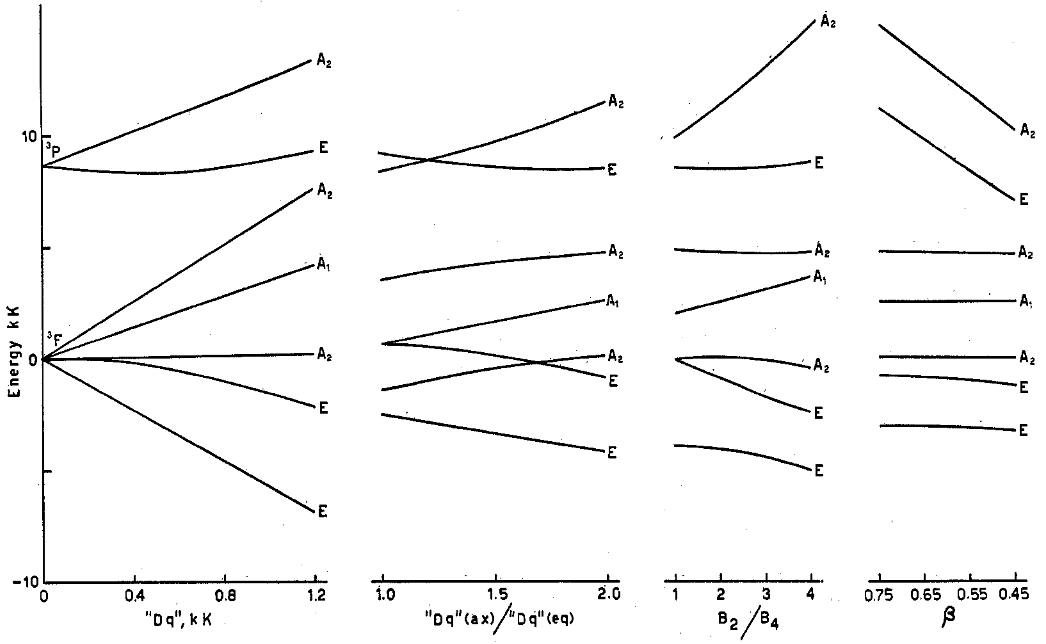

Figure 4.—Energy level diagram for a Ni(II) ion in C_{3v} symmetry: $Dq(\text{ax})/Dq(\text{eq}) = 2$; β, 0.55; $B_2/B_4 = 2$; average P–Ni–I angle, 140°. From the left the effect of relaxing the $Dq(\text{ax})/Dq(\text{eq})$ ratio, the B_2/B_4 ratio, and β is shown for $Dq(\text{eq}) = 0.75$ kK.

pared to I and the nephelauxetic β values for Br and I ($\beta_{\text{Br}} > \beta_{\text{I}}$). However, their splitting should decrease from the iodo to the bromo derivative, since the $Dq(\text{ax})/Dq(\text{eq})$ ratio should be smaller in the latter case. Actually only one band is strongly affected by the substitution of I with Br and an increase in splitting is observed. It seems more feasible therefore that the two F → P transitions are contained under the envelope of the 13.4 and 15.0 kK bands of the iodo and bromo derivatives, respectively, whereas the bands below 10 kK are due to F → F transitions. This assignment is supported by ligand-field calculations. In Figure 4 an energy level diagram for Ni(II) in C_{3v} symmetry is reported together with the effects of relaxing the B_2/B_4 radical integral ratio,[14] the $Dq(\text{ax})/Dq(\text{eq})$ ratio, and the nephelauxetic β parameter. Assuming a $Dq(\text{ax})/Dq(\text{eq})$ ratio > 1.5 ($Dq(\text{eq}) = 0.75$–0.8 kK[15] as expected for I and Br donor atoms[13]) and a β value of the order of 0.55 (β 0.50 was proposed for NiI_4^{2-} complex[16]), the F → P transitions are expected above 10 kK independently of the B_2/B_4 ratio value. A reasonable assignment, therefore, for the iodide derivative is $^3E \rightarrow {}^3E$ (<4.0 kK), $^3E \rightarrow {}^3A_2$ (5.6), $^3E \rightarrow {}^3A_1$ (7.8), $^3E \rightarrow {}^3A_2$ (9.4), $^3E \rightarrow {}^3E(P)$ (13.4), $^3E \rightarrow {}^3A_2(P)$ (13.4). A fifth band observed for the bromide derivative at 7.1 kK could be assigned to spin–orbit and low symmetry components of the excited levels or to a spin-forbidden transition stealing intensity *via* spin–orbit coupling. This assignment is consistent with that proposed by Quagliano, *et al.*, for the $NiNX_3$[9] chromophore and apart from the number of peaks observed is in substantial agreement with the assignment formerly proposed.[16,17] The agreement between expected and found transitions is not quite satisfactory, presumably because of geometrical effects and spin–orbit coupling effects. Such effects are expected to be strongly operative because all of the levels are close to each other.

The fact that the polarization properties cannot be interpreted on the basis of axial symmetry has to be ascribed to nonnegligible low symmetry components of ligand field. If spin–orbit coupling effects are also considered, the ^3E ground level will split into six levels, each of them interacting with ^3E and $^3A_1$ excited levels to different extents. Under these conditions some of these levels may be so close to the ground level that distribution of population occurs. Consequently the transition probability will be temperature dependent. The observed shifts of the frequency maxima (0.2–0.3 kK) are consistent with the present model. However, since the subgroups of C_{3v} nonretaining axial symmetry are only C_s or C_1 and spin–orbit coupling levels are hardly characterized in lack of detailed magnetic information, no attempt can be made to interpret the observed polarizations in more detail. It is interesting to note that the bands most affected by temperature are those assigned to transitions to orbitally nondegenerate A levels whose λ L.S. splittings are expected to be quite small. Therefore, such bands will be sensitive to the population of the ground level more than the transitions to the ^3E levels.

Although temperature dependent polarization changes have been reported,[18] the present ones are quite dramatic. Recently Dawson, *et al.*,[19] observed an increase in extinction coefficient and a decrease in splitting of bands with decreasing temperature in solution spectra of low-spin trigonal-bipyramidal nickel complexes. In this case, assuming C_{3v} symmetry, the expected ground level is orbitally nondegenerate; therefore the temperature dependent spectra were accounted for by dynamic Jahn–Teller effects operating on the excited E levels and/or by temperature dependent

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static distortions. In the present case an X-ray analysis has shown that a static distortion from C_{3v} symmetry is operative and this alone may account for the observed spectral properties.

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The Infrared Spectra of Ruthenium Derivatives of Nitrogen, Nitric Oxide, and Carbon Monoxide. Experimental Evidence Regarding dπ–pπ Bonding

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The infrared spectra of the compounds *trans*-[RuClNO(das)$_2$]Z$_2$ (Z$^-$ is Cl$^-$, Br$^-$, I$^-$, PF$_6^-$, $^1/_2$[PtCl$_6$]$^{2-}$, and das is *o*-phenylenebis(dimethylarsine)), *trans*-[RuINO(das)$_2$]Z$_2$, *trans*-[RuClN$_2$(das)$_2$]Z, and *trans*-[RuClCO(das)$_2$]Z have been investigated in the spectral region between 250 and 4000 cm^{-1}. The infrared spectra of the nitrosyl and dinitrogen complexes isotopically substituted with ^{15}N were prepared, and their spectra were utilized for identifying the fundamental vibrational modes of the RuXY moieties. Force constants for the RuXY groups were calculated using a three-body model and a valence force field. On the basis of these results, the band of medium intensity near 490 cm^{-1} in the dinitrogen complex, assigned by other workers to the Ru–N stretching vibration, has been reassigned to the RuNN bending vibration. This three-body model was also successfully applied to the analysis of the infrared spectrum of [Ru(NH$_3$)$_5$N$_2$]Br$_2$. The changes observed in the X–Y force constants upon coordination to ruthenium (Δk_{XY}) have a direct relationship to the ruthenium–ligand force constant, k_{RuX}. These observations are consistent with dπ–pπ bonding between ruthenium and the diatomic ligand.

Introduction

The infrared spectra of coordinated diatomic molecules are important both for elucidating the structures of these complexes and for obtaining information about the bonding between the metal and the ligand.[1–5] The numerous studies of carbon monoxide complexes are well known, and several careful investigations of the infrared spectra of transition metal nitrosyls have been carried out, including normal-coordinate analyses of these data.[6–10] However, only two papers have thus far appeared in which the infrared spectra of the coordinated dinitrogen ligand have been investigated in any detail.[11,12] Many of these earlier studies have been complicated by the presence of other similar ligands and ligand vibrations which may be strongly coupled to the motions of the diatomic molecule under consideration. In addition, there appear to be no comparative infrared studies of isostructural and isoelectronic complexes of the type L$_5$M–XY (where XY is CO, N$_2$, and NO and L is not).

In our previous work, the isostructural series of complexes *trans*-[RuClN$_2$(das)$_2$]$^+$, *trans*-[RuClNO(das)$_2$]$^{2+}$, *trans*-[RuClCO(das)$_2$]$^+$, and some of their ^{15}N-substitution products was prepared.[13] The infrared spectra of these compounds have now been obtained and are discussed below.

Experimental Section

Materials and Analyses.—Ruthenium and trichloronitrosylruthenium were obtained from Englehard Industries, Inc. The isotopically substituted compounds were prepared from ^{15}NO (95%) which was purchased from Bio-Rad Laboratories. Solvents and other common chemicals were obtained from Baker Chemical Co. and Mallinckrodt Chemical Works. The chemicals were of reagent grade and were not further purified unless noted. The elemental analyses were obtained from Huffman Laboratories, Wheatridge, Colo.; Chemalytics, Tempe, Ariz.; and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and are summarized in Table I. In the presence of ruthenium, the carbon analyses have been observed to be as much as 1% high.

Physical Measurements.—The nmr spectra were obtained using a Varian Model HA-100 or T-60 spectrometer and CDCl$_3$ or D$_2$O as solvent. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer which had been calibrated using polystyrene for the 350–3000-cm^{-1} region and the water band at 202.8 cm^{-1} for the 200–350-cm^{-1} region. A Du Pont curve resolver, Model 310, was used to separate overlapping peaks. The isotopic content of the nitrogen-containing complexes was established by mass spectrometry using a Perkin-Elmer Hitachi Model RMU-6e double-focusing mass spectrometer.

Preparation of the Complexes.—The unsubstituted complexes were prepared as described previously.[13] The ^{15}NO complexes were prepared from Ru(^{15}NO)Cl$_3$. Ruthenium trichloride as obtained from the manufacturers was found to be unreactive with NO. Consequently, RuCl$_3$ was prepared *in situ* and allowed to react with ^{15}NO to form Ru(^{15}NO)Cl$_3$. Ruthenium powder (1.00 g) was stirred for 12 hr together with 250 ml of 5% aqueous NaOCl. The solution was evaporated to 100 ml and cooled in an ice bath and 50 ml of concentrated hydrochloric acid was added followed by 50 ml of methanol. The volume of the solution was reduced by boiling, and after filtering, the filtrate was reduced to dryness in a 500-ml round-bottom flask. The solid material was dissolved in 100 ml of distilled water and 5 ml of concentrated hydrochloric acid. A total of 10.5 mmol

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