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Aryldiazo Complexes. Resonance Interaction of the N–N Stretching Vibration with Other Ligand Vibrational Modes

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Extensive isotopic labeling using ^{2}H and ^{15}N shows two or three bands which change frequency and intensity for many aryldiazo–transition metal complexes. This effect is shown to arise from the resonance interaction of ν(NN) with weak phenyl vibrational modes. From relative intensities of the respective bands, the unperturbed values of ν(NN) are estimated. A new cyclic polyether–benzenediazonium complex has been prepared and is shown to be the first diazo complex in which ν(NN) increases upon coordination.

Introduction

Aryldiazo ligands, as well as others which contain nitrogen–nitrogen multiple bonds, have been of great interest in recent years, especially because of their not-too-remote relationship to dinitrogen and nitrosyl ligands. Recently, several structural and synthetic studies involving aryldiazo or similar diazo ligands have been reported and show the reaction chemistry to be varied and interesting.[3-7]

Because knowledge of the electronic and structural environment of the diazo ligand would be useful in predicting and understanding the stability of new complexes and new reaction pathways, we hoped to derive some such information quickly and inexpensively by observing the infrared-active N–N stretching frequencies. The great difference in ν(NN) between the two ruthenium(II)–aryldiazo compounds $RuCl_3(N_2Ph)(PPh_3)_2$ (1882 cm^{-1}) and $RuCl(CO)_2(N_2Ph)(PPh_3)_2$ (1462 cm^{-1})[8] suggests that these stretching frequencies may be very useful as a means of characterizing M–N–N–Ph geometries and reactivities.

The appearance of multiple bands assignable to ν(NN) in the region of 1400–1600 cm^{-1} has been observed in unsymmetric, disubstituted diazenes, R'—N═N—R,[9,10] in symmetric diazenes (Raman study), R—N═N—R,[11] and in σ complexes of symmetric, trans diazenes.[12,13] It is not surprising then that we observe multiple bands in complexes of the type R—N═$\bar{N}$—M or R—N═N═M (M = metal).[14] With the exception of *cis*-azobenzene,[15] one finds in this region several bands, two to four of which could be associated with ν(NN). Most, if not all, of these bands move to lower energy in those cases when ^{15}N substitution is effected.[16] The isotopic shifts are relatively small, and the bands sometimes dramatically change relative intensities; some become too weak to be observed.

We now demonstrate for some aryldiazo–transition metal complexes that the two or more bands which shift on isotopic substitution result from resonance interaction of ν(NN) with weak vibrational modes of the attached phenyl group, not from cis and trans isomerism about the N–N multiple bond. Furthermore, we show how the approximate value of the unperturbed ν(NN) may be easily derived from the spectra without extensive isotopic labeling.

Experimental Section

All spectra were taken using a Perkin-Elmer 337 double-beam infrared spectrometer with a scale-expanding unit attached. The spectra were calibrated using a polystyrene film. Each spectrum was measured three times and averaged. The absolute frequencies are accurate to about ±5 cm^{-1}. Precision was ±2 cm^{-1}. Using a neighboring internal reference for a given compound with different isotopic labels, precision was ±1 cm^{-1} so that the difference between bands shifted by isotopic substitution is accurate to about ±2 cm^{-1}. Attempts were made to measure solution spectra in methylene chloride, but this was abandoned owing to slow to rapid decomposition in solution. Three mulling agents were used: Nujol for Rh complexes, hexachlorobutadiene for the Ir complex, and perfluorohydrocarbon for the Os complex. There was little if any decomposition in the mulls. The mull thickness and concentration were adjusted so that a reference peak for a given compound had approximately the same intensity for all of the isotopically substituted species. Relative intensities (A') were estimated by measuring peak heights and widths after conversion from transmittance to absorbance. Raman spectra were obtained using a unit containing a Spex 1401 double monochromator and a krypton ion laser. The samples, which were sealed under vacuum, were spun in 12-mm tubes and cooled to about 190°K to reduce decomposition. Power was 20–50 mW at the sample using the 6471-Å exciting line.

RhCl(ppp),[17] $RhCl_2(N_2Ph)(PPh_3)_2$,[5] $IrCl_2(CO)(N_2Ph)(PPh_3)_2$,[6] and $OsH(CO)(N_2Ph)(PPh_3)_2$[18] were prepared by literature techniques. The impure mixture of dicyclohexyl[18]-crown-6 isomers and aniline-d_5 (99+% ^{2}H) were purchased from Aldrich Chemical Co. The pure cis-anti-cis and cis-syn-cis isomers were separated and purified.[19] Benzenediazonium salts were prepared by usual techniques[20] from aniline and sodium nitrite and were carefully recrystallized from acetone–ethanol–diethyl ether to remove any traces of halide ion. The compounds $Na^{15}NO_2$ (95–97% ^{15}N) and aniline-^{15}N (95–99% ^{15}N) were purchased from Stohler Isotope Chemicals. Elemental analyses were performed by H. Beck at Northwestern's Analytical Services Laboratory.

Chloro(phenyldiazo)(phenylbis(3-diphenylphosphinopropyl)phosphine)rhodium(III) Hexafluorophosphate. This was prepared by a modification of the published procedure.[17] $[PhN_2][PF_6]$ (0.26 g) was stirred in 10 ml of absolute methanol for a few minutes until most of the diazonium salt dissolved. RhCl(ppp) (0.70 g) was added to the well-stirred mixture; the color of the slurry changed from yellow to orange within 1 or 2 min. The mixture was stirred an additional ten minutes, filtered, washed with methanol and ether, and dried *in vacuo* yielding bright orange microcrystals (94%). When recrystallized from dichloromethane–methanol, beautiful red-orange crystals of the 1:1 CH_2Cl_2 solvate resulted. *Anal.* Calcd for $C_{42}H_{42}RhN_2F_6P_4Cl$: C, 53.15; H, 4.46; N, 2.95. Found: C, 53.01; H, 4.56; N, 2.79.

(Dicyclohexyl[18]-crown-6)benzenediazonium Hexafluorophosphate. A solution containing 0.40 g of the purified cis-anti-cis isomer of the cyclic ether in 3 ml of acetone was mixed with a similar solution of 0.25 g of $[PhN_2][PF_6]$ in 2 ml of acetone. When the solution was allowed to sit quietly for 2 hr, large, well-developed prisms of the complex were deposited in about 50% yield. Alternatively, diethyl ether was added dropwise with stirring to the solution until it began to become cloudy. One additional milliliter of ether was added, and the mixture was cooled at −20° for 1 hr. To ensure complete crystallization, the volume of the mixture was doubled by addition of more ether, and the white, microcrystalline complex was filtered, washed with pentane, and dried *in vacuo*. The yield was 95%. The diazonium complex is soluble in chlorinated solvents.[21] *Anal.* Calcd for $C_{26}H_{41}N_2O_6F_6P$: C, 50.16; H, 6.64; N, 4.50. Found: C, 50.20; H, 6.51; N, 4.61.

Discussion

As can be seen from the four examples chosen for illustrative purposes (see Figure 1), all complexes show multiple bands in the 1400–1600-cm^{-1} region. In order to elucidate the origin of these infrared-active bands which are associated with ν(NN), the complexes were prepared with six different isotopic labels: C_6H_5–^{14}N–^{14}N, C_6H_5–^{14}N–^{15}N, C_6H_5–^{15}N–^{14}N, C_6H_5–

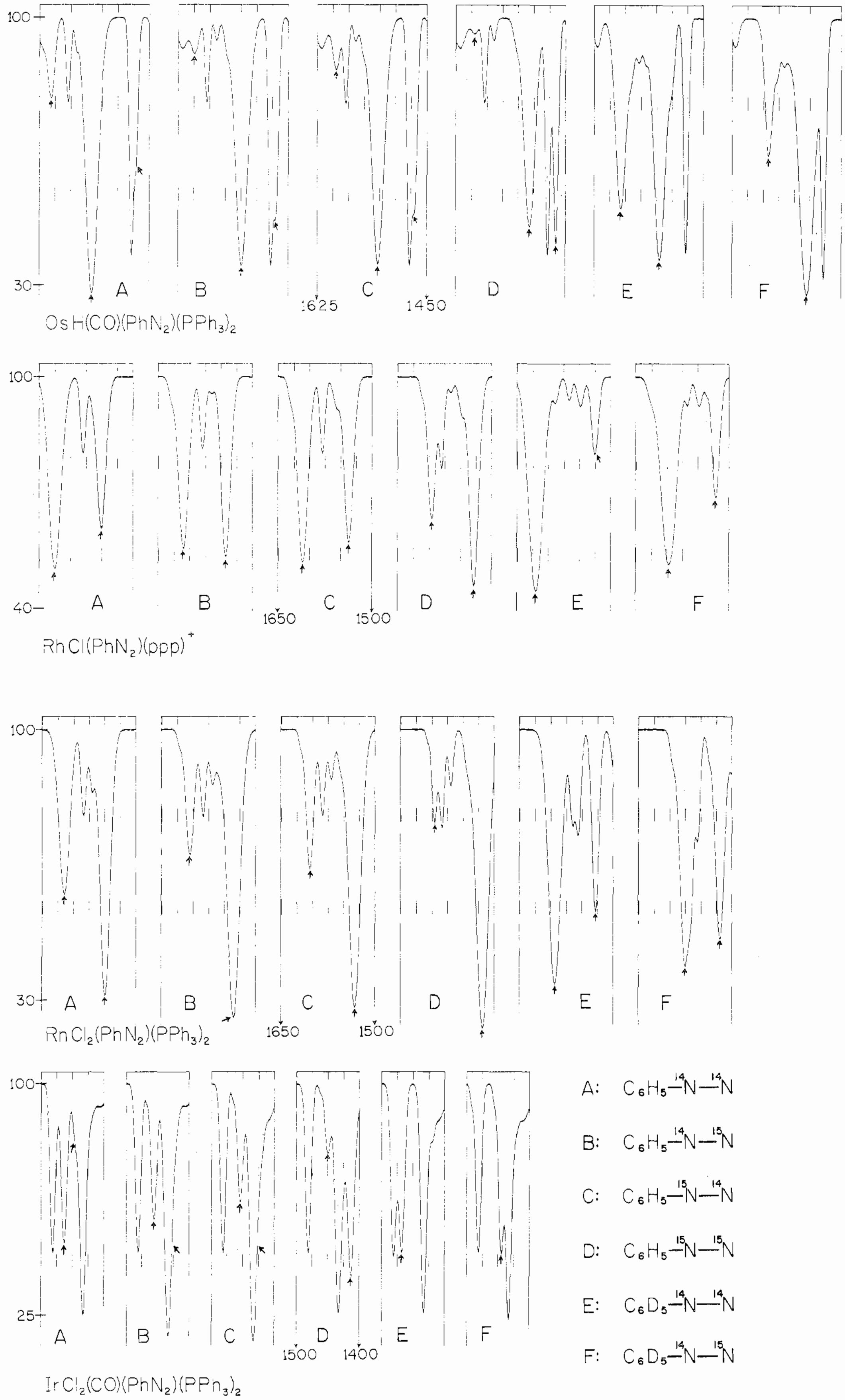


Figure 1. Computer-drawn spectra which were smoothed, corrected for a nonconstant base line, and scaled so that a reference peak for a given compound has the same intensity in each of the isotopically labeled species. Vertical axis is transmittance (%), and the horizontal axis is frequency (cm^{-1}). Arrows indicate bands associated with ν(NN).

Table I.[a] N–N Stretching Frequencies in Some Aryldiazo Complexes

Compd	Obsd ν(NN)	Δν(NN)[b]	Γ, intensity ratio	$E^0{}_1$, coupling freq[c]	$E^0{}_2$, calcd[c] ν(NN)	ν(NN)[c]	ν(NO)[d]
$\mathrm{[RhCl(L)(ppp)][PF_6]}$							
$\mathrm{L = C_6H_5{-}^{14}N{-}^{14}N}$	1550, 1624	(27, 56)	10:21	1574	1600	1600	1692[f]
$\mathrm{C_6H_5{-}^{14}N{-}^{15}N}$	1542, 1609	23	11:10	1577	1574	1601	
$\mathrm{C_6H_5{-}^{15}N{-}^{14}N}$	1537, 1610	27	10:12	1571	1576	1603	
$\mathrm{C_6H_5{-}^{15}N{-}^{15}N}$	1527, 1594	53	17:10	1569	1552	1606	
$\mathrm{C_6D_5{-}^{14}N{-}^{14}N}$	1525, 1619		10:54	1540	1604	1604	
$\mathrm{C_6D_5{-}^{14}N{-}^{15}N}$	1521, 1597	26	10:26	1542	1576	1603	
$\mathrm{RhCl_2(L)(PPh_3)_2}$							
$\mathrm{L = C_6H_5{-}^{14}N{-}^{14}N}$	1549, 1614	(27, 55)	15:10	1588	1575	1575	1630[g]
$\mathrm{C_6H_5{-}^{14}N{-}^{15}N}$	1535, 1604	24	34:10	1588	1551	1577	
$\mathrm{C_6H_5{-}^{15}N{-}^{14}N}$	1532, 1603	28	28:10	1585	1551	1577	
$\mathrm{C_6H_5{-}^{15}N{-}^{15}N}$	1518, 1594	51	99:10	1587	1525	1578	
$\mathrm{C_6D_5{-}^{14}N{-}^{14}N}$	1528, 1593		10:25	1546	1575	1575	
$\mathrm{C_6D_5{-}^{14}N{-}^{15}N}$	1519, 1575	27	10:18	1540	1555	1581	
$\mathrm{OsH(CO)(L)(PPh_3)_2}$							
$\mathrm{L = C_6H_5{-}^{14}N{-}^{14}N}$	1541, 1605, 1472[j]	(26, 54)	79:14:10	1595	1551	1551	1630[h]
	1472, 1541, 1605[j]		10:79:14	1480	1533	1533	
$\mathrm{C_6H_5{-}^{14}N{-}^{15}N}$	1469, 1524, 1598[j]	27	10:51:4	1478	1515	1541	
$\mathrm{C_6H_5{-}^{15}N{-}^{14}N}$	1469, 1528, 1595[j]	26	10:53:5	1478	1519	1545	
$\mathrm{C_6H_5{-}^{15}N{-}^{15}N}$	1465, 1507, 1595[j]	51	10:18:1	1480	1492	1544	
$\mathrm{C_6D_5{-}^{14}N{-}^{14}N}$	1519, 1581		14:10	1556	1544	1544	
$\mathrm{C_6D_5{-}^{14}N{-}^{15}N}$	1506, 1567	27	28:10	1555	1518	1544	
$\mathrm{IrCl_2(CO)(L)(PPh_3)_2}$							
$\mathrm{L = C_6H_5{-}^{14}N{-}^{14}N}$	1444, 1465	(25, 51)	10:90	1446	1463	1463	i
$\mathrm{C_6H_5{-}^{14}N{-}^{15}N}$	1433,[e] 1455	~21	10:18	1441	1447	1472	
$\mathrm{C_6H_5{-}^{15}N{-}^{14}N}$	1433,[e] 1454	~22	10:11	1443	1444	1469	
$\mathrm{C_6H_5{-}^{15}N{-}^{15}N}$	1412, 1450	47	30:10	1441	1422	1472	
$\mathrm{C_6D_5{-}^{14}N{-}^{14}N}$	1468				1468	1468	
$\mathrm{C_6D_5{-}^{14}N{-}^{15}N}$	1445	23			1445	1470	

[a] Frequencies are given as wave numbers (cm^{-1}). [b] The sum of the differences for all the bands which shift. In parentheses are the calculated shifts for one and two ^{15}N atoms, respectively. [c] See text for calculations. [d] For corresponding nitrosyl complexes. [e] Approximate value. [f] Reference 17. [g] S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1254 (1971). [h] B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Dalton Trans.*, 478 (1973). [i] Analogous nitrosyl complex not known. [j] This band was ignored during calculations.

^{15}N–^{15}N, $\mathrm{C_6D_5}$–^{14}N–^{14}N, and $\mathrm{C_6D_5}$–^{14}N–^{15}N. As can be seen from the spectra, two or three bands dramatically shift and change intensity with isotopic substitution. The infrared intensities of these bands, relative to other bands, are stronger than the corresponding Raman intensities. Indeed, in many instances, some of the bands could not be observed at all in the Raman spectra.

Generally, for a resonance interaction to occur between a fundamental vibration (usually strong) and another fundamental, overtone, or combination band, the interaction must be allowed by symmetry, the two bands must be near one another in energy, and vibrations must involve atoms which are reasonably close together, *i.e.*, kinematic coupling. These conditions are frequently fulfilled for the aryldiazo ligand.

If there is a resonance interaction between two vibrational modes, the energies of the unperturbed states may be calculated. Assuming that only two modes are interacting and that one of them has negligible intrinsic intensity, one may apply the following formulations of Overend[22]

$$E^0{}_2 = {}^1\!/_2(E_2 + E_1 + E_\mathrm{d})$$

$$E^0{}_1 = {}^1\!/_2(E_2 + E_1 - E_\mathrm{d})$$

where

$$E_\mathrm{d} = (E_2 - E_1)(R - 1)/(R + 1)$$

$$R = \Gamma_2/\Gamma_1 \approx A_2{}'E_1/A_1{}'E_2$$

Here E_1, E_2, A_1', and A_2' are the observed energies and integrated intensities of the two bands; $E^0{}_2$ is the energy of the unperturbed band with intrinsic intensity, and $E^0{}_1$ is the energy of the unperturbed band without intrinsic intensity.[23] When these equations are applied to the experimental data, remarkably good results are obtained (Table I). The unperturbed bands with intrinsic intensity ($E^0{}_2$) change upon isotopic substitution and the others without intrinsic intensity ($E^0{}_1$) do not. Those that change move in the proper direction to lower energy and move the correct amount assuming that the N–N vibration obeys the diatomic, harmonic oscillator approximation. The values of ν(NN) were obtained by multiplying $E^0{}_2$ by 1.000, 1.017, or 1.035 depending upon the isotopic substitution, *i.e.*, zero, one, or two ^{15}N atoms, respectively. Considering experimental accuracies and the assumptions made, the constancy of $E^0{}_1$ and ν(NN) is remarkable. It is clear from these data that, as expected, the coupling frequencies from the $\mathrm{C_6H_5}$ group are different from $\mathrm{C_6D_5}$, yet the N–N stretching frequencies are essentially the same for a given compound. We find that, depending on the accuracy that is desired, the values of the unperturbed energies are dependent on the accuracies of E_1 and E_2 and especially on their difference but less so on the magnitudes of the relative intensities. Fortunately, only the relative intensities of two bands near each other in the same spectrum must be known. Thus, many possible errors in measurement tend to cancel, and the measurement of infrared intensities in mull spectra, though fraught with problems and inaccuracies, is sufficiently good for these purposes. It should be noted here that there is no solid-state splitting of the observed bands since all of them also appear in solution spectra with about the same relative intensities. Furthermore, from limited data there appears to be little coupling between ν(NN) and ν(CO) or ν(MH) in carbonyl and hydrido complexes.

The differences in the spectra for complexes of Ph–^{14}N–^{15}N and Ph–^{15}N–^{14}N are relatively small. This observation supports the assumption which has been made, namely, that the isotopic shifts for $E^0{}_2$ can be calculated to a first approximation using the diatomic, harmonic oscillator model, despite the obvious fact that a phenyl group and a heavy metal are both attached to the N_2 unit. One might expect that the complex with the ^{15}N attached to the phenyl, in comparison with the complex with the ^{15}N attached to the metal, would show greater isotopic shifts in those bands closer to the $E^0{}_1$ values because of the greater involvement of the phenyl nitrogen atom in the kinematic coupling. This effect is observed in many of the complexes but not in others; the accuracy of the experimental data do not warrant a definite conclusion.

It appears as though the observed resonance coupling occurs with fundamental modes since frequently reoccurring coupling frequencies belonging to the C_6H_5 group occur near 1440, 1480, and 1580 cm^{-1} and those belonging to C_6D_5 occur near 1550 cm^{-1}. In benzenediazonium hexafluorophosphate bands appear near 1465, 1570, and 1580 cm^{-1} which are shifted in the perdeuterated analog to 1310, 1525, and 1555 cm^{-1}. For diazo complexes containing both PPh_3 and PEt_3, in which ν(NN) is too far away to couple, these frequencies occur near 1445–1450, 1565–1575, and 1575–1585 cm^{-1} for C_6H_5 and near 1340–1350, 1525–1535, and 1545–1555 cm^{-1} for C_6D_5. Although the first two bands in the free diazonium salts are strong in intensity and the third is weak, all three appear to be weak in intensity when the ligand is complexed to a metal. Thus, if indeed ν(NN) is coupling with fundamentals and not combination or overtone bands, then the assumption that the coupling bands have negligible intrinsic intensities is valid to a first approximation. Furthermore, there are four weak phenyl absorptions in the diazonium salts between 1930 and 2040 cm^{-1} which could account for the coupling at high energies.

Of primary interest is the aryldiazo complex of rhodium [RhCl(ppp)(N_2Ph)][PF_6] whose solid-state structure is known with certainty.[4] Two bands near 1550 and 1625 cm^{-1} appear in the mull spectra of powders of the solvated (CH_2Cl_2) and unsolvated complex, as well as in crushed single crystals of the solvated complex. Indeed, a thin, platelike single crystal of the solvated complex, whose space group and cell dimensions were identical with those of the single crystal used in the X-ray analysis, showed these two bands in its transmission infrared spectrum. Because there was no disorder or cis–trans isomerism about the N–N double bond observed in the structural study, nor could such isomers exist for steric reasons, we felt that the appearance of the two bands resulted from Fermi resonance or another resonance interaction. This was demonstrated by extensive isotopic substitution using ^2H and ^{15}N in the unsolvated complex. In view of the environment of the metal, a value 1603 cm^{-1} for ν(NN) (ν' 1523 cm^{-1})[4] is reasonable for a doubly bent diazo ligand. Unlike many other 16- and/or 18-electron, five-coordinate, cationic aryldiazo complexes, this one does not add Cl^- easily, although HCl is easily added. Thus, the reluctance to add Cl^- is apparently caused by electronic rather than steric factors. Although we formulate this complex as though it contains Rh(III) in a formal sense, the foregoing observations suggest that the rhodium atom is not effective at completely transferring two of its electrons (forming a 16-electron complex) to the diazo ligand and that the observed and modified[4] N–N stretching frequencies represent upper limits for doubly bent ligands.

A similar rhodium–aryldiazo complex, $RhCl_2(N_2Ph)(PPh_3)_2$, also shows two bands. The coupling frequencies for both perdeuterated rhodium complexes are the same, 1541 *vs.* 1543 cm^{-1}, while those for both ^1H complexes differ by a small amount, 1573 *vs.* 1587 cm^{-1}. It is comforting to find that N–N stretching frequencies in the same region apparently couple with the same or similar vibrational modes. It is not certain at this point, despite the apparent self-consistency of the data, whether 1573 and 1587 cm^{-1} are statistically and significantly different considering the errors inherent in the measurements and calculations and considering the possible changes in the phenyl modes within different complexes.

The iridium–aryldiazo complex $IrCl_2(CO)(N_2Ph)(PPh_3)_2$, in which the diazo ligand acts as a one-electron donor (doubly bent geometry), illustrates several interesting points. Most striking is the appearance of only one band in the perdeuterated species, which shifts the expected amount upon ^{15}N substitution. Here ν(NN) has been decoupled from interacting phenyl modes. In the unperdeuterated complexes the detection of the lower energy band is masked by strong phenyl absorptions from the triphenylphosphine ligand. Inspection of the spectra shows a distinct shoulder at 1444 cm^{-1} when two ^{14}N atoms are present. This shoulder disappears upon ^{15}N substitution. When one ^{14}N atom is present, the 1433-cm^{-1} band, normally attributed to the phosphine phenyl modes, is distinctly and reproducibly more intense than in any of the other complexes (Figure 1). Of course, with two ^{15}N atoms both bands appear clearly. A value of 1470 cm^{-1} (ν' 1470 cm^{-1}) for ν(NN) is in the range to be expected for a neutral, six-coordinate, doubly bent aryldiazo complex. The observed band at 1465 cm^{-1} (ν(NN) 1463 cm^{-1}) is distinctly lower than the others. This effect is probably caused by a small, additional coupling interaction with a diazo phenyl mode near 1480 cm^{-1}. The 1481-cm^{-1} band in the spectrum, primarily resulting from a phosphine phenyl mode, is somewhat more intense than that band in the other species, but by an amount only slightly larger than the precision in measuring the intensity of this band.

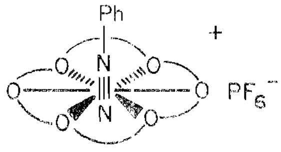
Finally the osmium complex $OsH(CO)(N_2Ph)(PPh_3)_2$ shows three distinct bands which change position and intensity upon isotopic substitution. Fortunately, except for the unsubstituted compound, the highest energy band is of sufficiently low intensity so that it may be neglected for the sake of these approximate calculations. Because there are no strong phosphine phenyl modes nearby, this weak band may be seen in these spectra. Because the 1605- and 1472-cm^{-1} bands are almost equally disposed about the intense central band and because they are of similar intensity, the intense 1541-cm^{-1} band is probably very near the uncoupled value of ν(NN). If one performs the respective calculations, first neglecting the lowest energy band and then the highest energy band, one obtains values of $E^0{}_2$ of 1551 and 1533 cm^{-1}, respectively, the average of which at 1542 cm^{-1} is very near both the central intense band at 1541 cm^{-1} and the average of ν(NN) at 1543 cm^{-1} obtained from the isotopically substituted species in which the intensity of the highest energy band is very small. Although the reaction chemistry (addition of $HClO_4$) suggests that the complex contains a doubly bent PhN_2^- ligand with concomitant square-pyramidal geometry, the resulting trans arrangement of hydrido and carbonyl ligands is unfavorable in this type of five-coordinate complex. Thus we believe this complex to have a trigonal-bipyramidal geometry with trans phosphine ligands. Structural work is in progress to clarify this point.

The spectra of the osmium complexes are similar to and typical of those of the isoelectronic series $RuX(CO)(N_2Ph)(PPh_3)_2$ (X = Cl, H) and $OsX(CO)(N_2Ph)(PPh_3)_2$[18] (X = Cl, Br, H). It will be interesting to compare these with $FeX(CO)(N_2Ph)(PPh_3)_2$ (X = Cl, Br, N_3) which have been prepared by Lalor and coworkers.[25] Also, the iridium complex is similar to the unstable $RhCl_2(CO)(N_2Ph)(PPh_3)_2$,[18] to $IrXY(Z)(N_2Ph)(PPh_3)_2$[6] (X = Cl, Br, I, NCO, N_3, NO_2; Y = Cl, Br; Z = CO, NH_3, py, C_2H_5NC), and to $MX(CO)_2(N_2Ph)(PPh_3)_2$[18] (M = Os, Ru; X = H, Cl, Br, I, NCO).

In which region of the infrared spectrum does one expect to find coupling between the phenyl modes and ν(NN) of the phenyldiazo ligand? After observing dozens of complexes, the following generalizations can be made. Obvious coupling occurs in all complexes where ν(NN) is in the region 1400–1600 cm^{-1}. Coupling is frequently observed in the 1600–1680-cm^{-1} region to a lesser degree. If ν(NN) is more than 100 cm^{-1} away from a coupling frequency, no coupling is observed; if it is less than 50 cm^{-1} away, coupling is observed.

Experimentally, the presence of the coupling interaction can be detected in two ways. (1) Coupling is probably present when the isotopic shift or sum of isotopic shifts is significantly less than that calculated using an estimated value of ν(NN). Thus for $RhCl(N_2Ph)(ppp)^+$, the sum of the shifts for the $C_6H_5{-}^{14}N{-}^{15}N$ complex is 23 cm^{-1}, and the calculated shift is 27 cm^{-1}. However, the same shift for the easily visible high-energy band in $IrCl_2(CO)(N_2Ph)(PPh_3)_2$ is only 10 cm^{-1} (calculated is 25 cm^{-1}); thus, the presence of a second band was suspected and indeed found. (2) Coupling is probably present when there is a significant change of intensity in a band upon isotopic substitution. The change in intensity is sometimes easier to detect than the change in frequency. The low-energy band in the $C_6D_5{-}^{14}N{-}^{15}N$ complex for the above rhodium compound shows intensity enhancement by a factor of 1.7, but the change in frequency is only 4 cm^{-1}.

Interestingly, at very high energies coupling is again observed. Whereas there is no observed coupling in $IrCl(N_2Ph)(PPh_3)_2^+$ [6] (1868 cm^{-1}) or in $RuCl_3(N_2Ph)(PPh_3)_2$[5,6] (1882 cm^{-1}), multiple bands are observed in $RhCl(N_2Ph)(PPh_3)_2^+$ [4,18] near 1900, 1930, and 1980 cm^{-1} and in $RuCl(N_2Ph)(bipy)_2^{2+}$ [7] near 2000 and 2080 cm^{-1}. To investigate this further, a new cyclic polyether adduct of the benzenediazonium cation was prepared.[26] Here the donor–acceptor relationship has been reversed, and this complex of the cis-anti-cis isomer of dicyclohexyl[18]-crown-6 is the first complex in which the value of ν(NN) is observed to *increase* upon coordination to a value of 2317 cm^{-1}; in the free diazonium cation it occurs at 2285 cm^{-1}. However, in this complex and in several free diazonium salts, no coupling was observed. Thus in the region between 1900 and 2100 cm^{-1}, coupling appears to take place also, though it is less well documented.



The doubly bent geometry seems to facilitate kinematic coupling, but this is by no means necessary. Indeed the singly bent N_2Ph^+ complexes of Re(I), W(0), and Mo(0), such as $ReCl_2(N_2Ph)P_3$, $WCl(N_2R)P_4$,[27] and $MoCp(CO)_2(N_2Ph)$, may well show coupling with phenyl modes because the values of ν(NN) in these complexes are somewhat lower owing to the slight strengthening of the metal–nitrogen bond and concomitant weakening of the nitrogen–nitrogen bond.

We believe the above considerations are useful, indeed essential, for the determination of the unperturbed values of N–N stretching frequencies in diazo complexes. Because of the fewer and more conveniently located coupling frequencies in the perdeuterated phenyldiazo group and because aniline-d_5 is reasonably inexpensive and readily available, we routinely use the perdeuterated ligands in much of our synthetic work. With a single ^{15}N substitution one may determine if there is resonance coupling and which bands are involved and then make two independent calculations of E^0_1 and E^0_2. One can be reasonably certain that the observation of only one band in the 1400–1600-cm^{-1} region which shifts only 8–16 cm^{-1} upon replacement of one ^{14}N by ^{15}N indicates that there is a resonance interaction and that there probably is another band nearby in the spectrum which also shifts.

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Registry No. $[RhCl(PhN_2)(ppp)][PF_6]$, 50896-06-5; $RhCl_2(PhN_2)(PPh_3)_2$, 36581-26-7; $OsH(CO)(PhN_2)(PPh_3)_2$, 53608-71-2; $IrCl_2(CO)(PhN_2)(PPh_3)_2$, 41527-12-2; (dicyclohexyl[18]-crown-6)benzenediazonium hexafluorophosphate, 53608-72-3; RhCl(ppp), 34964-03-9.

References and Notes

(1) Northwestern University.
(2) The Ohio State University.
(3) D. Cashman and F. J. Lalor, *J. Organometal. Chem.*, **32**, 351 (1971); W. E. Carroll and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1754 (1973); W. E. Carroll and F. J. Lalor, *J. Organometal. Chem.*, **54**, C37 (1973); M. E. Deane and F. J. Lalor, *ibid.*, **57**, C61 (1973); M. E. Deane and F. J. Lalor, *ibid.*, **67**, C19 (1974); E. W. Abel, C. A. Burton, M. R. Churchill, and K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 268 (1974); R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Amer. Chem. Soc.*, **96**, 260 (1974); G. A. Heath, R. Mason, and K. M. Thomas, *ibid.*, **96**, 259 (1974); G. W. Parshall, *ibid.*, **89**, 1822 (1967); S. Cenini, R. Ugo, and G. LaMonica, *J. Chem. Soc. A*, 3441 (1971); A. J. Deeming and B. L. Shaw, *ibid.*, 1128 (1969); M. C. Baird and G. Wilkinson, *ibid.*, 856 (1967); G. Avitable, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, **27**, 725 (1971); J. A. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, **12**, 1676 (1973); R. B. King and M. B. Bisnette, *ibid.*, **5**, 300 (1966); R. B. King and M. S. Saran, *ibid.*, **13**, 364 (1974); M. L. H. Green, T. R. Sanders, and R. N. Whiteley, *Z. Naturforsch. B*, **23**, 106 (1968); A. N. Nesmeyanov, Y. A. Chapovskii, N. A. Ustynyuk, and L. G. Makarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 449 (1968); J. A. McCleverty and R. N. Whiteley, *Chem. Commun.*, 1159 (1971); D. R. Fisher and D. Sutton, *Can. J. Chem.*, **51**, 1697 (1973); J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, *J. Chem. Soc. A*, 2631 (1971); J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1010 (1972); J. Chatt, G. A. Heath, and G. J. Leigh, *ibid.*, 444 (1972); J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 612 (1973); J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Organometal. Chem.*, **57**, C67 (1973); S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969); S. Trofimenko, *J. Amer. Chem. Soc.*, **92**, 5118 (1970); M. F. Lappert and J. S. Poland, *Chem. Commun.*, 1061 (1969).
(4) A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Amer. Chem. Soc.*, **95**, 6859 (1973).
(5) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 176 (1973); K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 2713 (1973).
(6) B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3052 (1973).
(7) W. F. Little and W. L. Bowden, personal communication; see W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, **95**, 5084 (1973).
(8) The following abbreviations have been used: Ph = C_6H_5, Et = C_2H_5, P = mono(tertiary phosphine), ppp = $PhP(CH_2CH_2CH_2PPh_2)_2$, bipy = 2,2'-bipyridine, Cp = C_5H_5, py = pyridine.
(9) R. Kübler, W. Lütke, and S. Weckherlin, *Z. Elektrochem.*, **64**, 650 (1960).
(10) J. A. Carroll, D. R. Fisher, G. W. Rayner-Canham, and D. Sutton, *Can. J. Chem.*, **52**, 1914 (1974).
(11) J. Brandmüller, H. Hacker, and H. W. Schrötter, *Chem. Ber.*, **99**, 765 (1966).
(12) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2247 (1969).
(13) L. A. Kazitsyna, N. B. Kupletskaya, V. A. Ptitsyna, M. N. Bochkareva, and O. A. Reutov, *Vestn. Mosk. Univ., Khim.*, **21**, 117 (1966).
(14) Resonance interaction and multiple bands have also been observed in the Raman spectra for a large number of *cis*-phenyldiazene (phenyldiimide) complexes: B. L. Haymore and J. A. Ibers, submitted for publication.
(15) Here there is only one band, ν(NN) 1511 cm^{-1}, whose isotopic shift is large when one ^{14}N atom is replaced by an ^{15}N atom (25-cm^{-1} shift measured, 26-cm^{-1} shift calculated); see ref 9.
(16) For ^{15}N isotopic studies on NO and N_2 ligands see S. Pell, R. H. Mann, H. Taube, and J. N. Armor, *Inorg. Chem.*, **13**, 479 (1974); E. Miki, K. Mizumachi, T. Ishimori, and H. Okuno, *Bull. Chem. Soc. Jap.*, **46**, 3779 (1973); J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, **93**, 1788 (1971); A. D. Allen, F. Bottomley, R. D. Harris, V. P. Reinsalu, and C. V. Senoff, *ibid.*, **89**, 5595 (1967); J. Chatt, A. B. Nikolsky, R. L. Richards, J. R. Sanders, J. E. Fergusson, and J. L. Love, *J. Chem. Soc. A*, 1479 (1970).
(17) T. E. Nappier, D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 4194 (1973).
(18) B. L. Haymore and J. A. Ibers, to be submitted for publication.
(19) B. L. Haymore, M.Sc. Thesis, Brigham Young University, Provo, Utah, 1971, p 32.
(20) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York, N.Y., 1956, p 609.
(21) G. W. Gokel and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 481 (1973).
(22) J. Overend in "Infra-red Spectroscopy and Molecular Structure," M. Davis, Ed., American Elsevier, New York, N.Y., 1963, p 350.

(23) There is not a large difference between ratios of Γ which is proportional to $\int A(\nu)\, d \ln \nu$ and A' which is proportional to $\int A(\nu)\, d\nu$, but since $\Gamma \simeq A'/E_{max}$, the correction was easily applied. $A(\nu) = -\log T(\nu)$ and $T(\nu) = I(\nu)/I_0(\nu)$ where E_{max} is the energy at the peak maximum, A is absorbance, T is transmittance, and I and I_0 are the intensities of the incident radiation at each frequency with and without absorption by the sample.

(24) By analogy to chlorobenzene, one would expect to find four bands (two A_1 and two B_2 for C_{2v} symmetry) near 1580 (two bands), 1480, and 1450 cm^{-1} which shift upon perdeuteration to 1560, 1540, 1350, and 1320 cm^{-1}. These all are loosely assignable to the in-plane modes corresponding to C–C vibrations; see T. R. Nanney, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, **21**, 1495 (1965). A band at 1480 cm^{-1} appears in chlorobenzene and in triphenylphosphine, but it is not observed in the diazonium salts, nor could it be observed in the complexes owing to interfering absorptions. L. S. Gray, V. A. Fassel, and R. N. Kniseley, *Spectrochim. Acta*, **19**, 514 (1960), reported a band at 1500 cm^{-1} which shifts upon ^{15}N substitution in KBr pellets of benzenediazonium chloride, but we cannot detect this band in mulls of the hexafluorophosphate salts.

(25) W. E. Carroll, F. A. Deeney, and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1430 (1974).

(26) This cyclic ether complex is especially useful from a synthetic standpoint since it is quite soluble in chloroform and methylene chloride, whereas the free diazonium salt is insoluble in these solvents.

(27) We are considering the conditions under which the diazo ligand is monodentate.

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Thermodynamics of Solvation of the Copper(II) Acetate Dimer[1]

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The potential difference between Cu(Hg) and Hg–$Hg_2(OAc)_2$ electrodes has been measured for a wide range of $Cu(OAc)_2$–H_2O–HOAc solutions. $E° = 0.2917 \pm 0.0003$ V for the cell reaction $2Cu(Hg) + 2Hg_2(OAc)_2(s) + 2H_2O(l) = Cu_2(OAc)_4 \cdot 2H_2O(s) + 4Hg(l)$. This corresponds to $G° = -447.35$ kcal mol^{-1} for the solid $Cu_2(OAc)_4 \cdot 2H_2O$. Similarly measurements for solid $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$ give $E° = 0.2983 \pm 0.0007$ V and $G° = -634.36$ kcal mol^{-1}. Extensive spectrophotometric measurements of the solubility of $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$ give $G° = -329.12 - 0.293(H_2O) + 0.0365(H_2O)^2 - 0.00183(H_2O)^3$ for the free energy of the $Cu_2(OAc)_4$ dimer in acetic acid solutions as a function of the water concentration. Approximate enthalpies and entropies are calculated for the various solids and for the monomeric and dimeric forms of copper acetate in solution. In both solids and in solution the copper acetate dimer shows a clear preference ($\Delta G° = -0.9 \pm 0.3$ kcal mol^{-1}) for the coordination of water as opposed to acetic acid. New equations are given for the activities in the system water–acetic acid.

There are three solid species present in equilibrium with acetic acid–water solutions saturated with copper acetate at 25°. Over the range from 14.97 M water to pure water one has the well-known $Cu_2(OAc)_4 \cdot 2H_2O$, containing the dimeric $Cu_2(OAc)_4$ group with four bridging acetate ions and the two water molecules as axial ligands.[2] Below 0.50 M H_2O, $Cu_2(OAc)_4 \cdot 2HOAc$[3,4] is stable, and a third solid forms at intermediate water concentrations. One is tempted to formulate the third solid by analogy to the other two as $Cu_2(OAc)_4 \cdot H_2O \cdot HOAc$ as has been done in the recent literature,[5] in spite of the old analytical data of Sandved[3] corresponding to $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$. This work establishes that Sandved's formulation is correct and provides thermodynamic values for all three solids based upon solubility data and potentiometric measurements with the Cu(Hg) and Hg–$Hg_2(OAc)_2$ electrodes in saturated solutions.

The Formulation of $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$. For solutions saturated with $Cu_2(OAc)_4 \cdot nH_2O \cdot mHOAc$ the Nernst equation takes the form

$$E = E° + (0.05916/4) \log (a_{H_2O})^n (a_{HOAc})^m$$

It was found that the variation of the potential with the water concentration in this region was not fitted by the value $n = 1$, so it was necessary to check the formula of the solid formed. A sample of 0.0709 mol of $Cu_2(OAc)_4 \cdot 2H_2O$ was stirred with 20.0 ml of glacial acetic acid in a volumetric flask suspended in a water bath at 25°. After equilibration including complete recrystallization of the solid, a sample of the supernatant was analyzed spectrophotometrically and found to be 0.53 M H_2O. The acetic acid used was 0.19 M in water, and the small increase observed can easily be due to incorporation of some of the acetic acid into the solid. If even one-fourth of the water present in the original solid were released upon recrystallization, the water concentration would be over 1.8 M in the supernatant. This simple experiment confirms that $n = 2$ as reported by Sandved.[3]

It is a little harder to determine the amount of acetic acid present in the solid formed, but it can be estimated indirectly by the increase in water concentration as the acetic acid is removed. Thus similar experiments with 1.0 ml of water present initially give $m = 2 \pm 0.4$.

Potentiometric Measurements on Saturated Solutions. As described in the Experimental Section, the best measurements with the Cu(Hg) and Hg–$Hg_2(OAc)_2$ electrodes were obtained with solutions saturated with either $Cu_2(OAc)_4 \cdot 2H_2O$ or $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$. For the second of these solids the cell reaction is $2Cu(Hg) + 2Hg_2(OAc)_2 + 2H_2O + 2HOAc = 4Hg(l) + Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc(s)$ and the Nernst equation takes the form

$$E = E° + (0.05916/4) \log (a_{H_2O})^2 (a_{HOAc})^2$$

To correct the observed potentials to $E°$ one needs the activities of water and acetic acid at each water concentration. These are readily calculated from the mole fractions using the formulas of Hansen, Miller, and Christian,[6] provided one assumes that the addition of copper acetate does not appreciably affect the activities. This is undoubtedly a poor assumption at high water concentrations where the solubility of copper acetate approaches 6.79%,[3] but it should be reasonable over the range from 0 to 19 M H_2O where the solubility is less than 1% by weight.

Table I shows the $E°$ values obtained in this way from the observed potentials over a range of water concentrations, with the value $E° = 0.2983 \pm 0.001$ V obtained by averaging the best values. This corresponds to $G° = -634.36$ kcal mol^{-1} for solid $Cu_2(OAc)_4 \cdot 2H_2O \cdot 2HOAc$.

It is difficult to interpret the data at extremely high water concentrations, so the best data on solutions saturated with $Cu_2(OAc)_4 \cdot 2H_2O$ are at the driest point at 19.0 M H_2O. This solution gave $E = 0.2874$, $E° = 0.2917$ V, and $G° = -447.35$ kcal mol^{-1} for solid $Cu_2(OAc)_4 \cdot 2H_2O$.

From these two free energy values we can calculate $K =$