TABLE I

p-NITROPHENOXY-SUBSTITUTED PHOSPHONITRILES

		Mp, °C	Yield, %	% calcd					% found					Mol wt	
				C	H	Cl	N	P	C	H	Cl	N	P	Calcd	Found
I	$(PN)_3(p\text{-}NO_2\cdot C_6H_4O)_6$	263–264	87	44.87	2.51	...	13.08	9.64	45.06	2.61	...	13.21	9.45	963.6	
II	$(PN)_3Cl(p\text{-}NO_2\cdot C_6H_4O)_5$	183–184	~0.7	41.80	2.35	...	13.02	10.80	41.97	2.50	...	13.11	10.90	861.0	
III	$(PN)_3Cl_3(p\text{-}NO_2\cdot C_6H_4O)_3$	225–226	~1.0	32.95	1.83	...	12.80	14.18	32.72	1.88	...	12.99	14.36	655.8	
V	$(PN)_3Cl_5\text{-}p\text{-}NO_2\cdot C_6H_4O$	95–97	17	16.00	0.90	39.36	12.44	20.64	16.20	0.89	39.40	12.54	20.48	450.6	
VI	$(PN)_4(p\text{-}NO_2\cdot C_6H_4O)_8$	299–301	79	44.87	2.51	...	13.08	9.64	45.09	2.31	...	13.10	9.54	1284	1275

g (0.5 mole) of $(PNCl_2)_3$ in 500 ml of toluene. After refluxing for 7 hr, the white precipitate was separated by filtration, and the filtrate was freed from solvent and fractionated. Compound V distilled at about 165° (0.02 mm). It was further purified by recrystallization from *n*-heptane to yield 38.3 g of pure V.

The filter cake—mostly triethylamine hydrochloride—was dissolved in water, and the insoluble portion was separated and dried. Recrystallization from dimethylformamide gave 12.8 g of pure VI.

2-Chloro-2,4,4,6,6-pentakis(*p*-nitrophenoxy)phosphonitrile (II) and 2,4,6-Trichloro-2,4,6-tris(*p*-nitrophenoxy)phosphonitrile (III).—An amount of 483.3 g (3.0 moles) of sodium *p*-nitrophenoxide was stirred in 1500 ml of refluxing xylene, and 138.9 g (0.40 mole) of trimeric phosphonitrilic chloride dissolved in 400 ml of xylene was added dropwise. Refluxing was continued for 31.5 hr after addition of the chloride was completed. The cooled product was washed with water. Removal of the xylene *in vacuo* rendered 183 g of a dark brown resinous material. This product was dissolved in 600 ml of warm toluene. A small amount of an undissolved white solid, mp 220–238°, was filtered off. The filtrate was concentrated to approximately half of its original volume. The concentrate deposited a small amount of solid, mp 177–216°, upon standing for 3 days. This product was recrystallized twice from toluene, once from 50% toluene–chloroform, and finally from toulene to give 2.1 g of pure II.

Small amounts of solids remained undissolved in each recrystallization of II. These were combined with the material melting at 220–238° and recrystallized from chloroform, in the presence of activated carbon, to give 2.9 g of pure III.

Acknowledgment.—This search was supported by the U. S. Navy, Bureau of Ships, as part of Project NObs 90092.

Correspondence

The Role of ν(C–N) as Evidence for the Mode of Binding of Amides to Lewis Acids

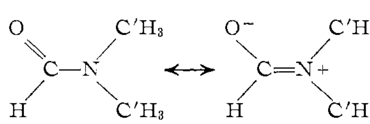
Sir:

While investigating the action of Lewis bases on the esterification of halides of elements in group IV,[1] we became interested in the application of evidence from infrared spectroscopy to the problem of determining whether, in amide adducts, the amide is coordinated through oxygen or nitrogen.

Nmr studies of amides show conclusively that the carbonyl oxygen is the stronger base toward the proton[2] and toward boron trichloride,[3] and a crystallographic study of formamide and acetamide complexes with bivalent metal ions has shown that the amide is bonded to the metal through oxygen.[4,5]

Apart from the studies mentioned above, other cases to be found in the literature are argued from infrared evidence, using ideas first put forward by Penland, Mizushima, Curran, and Quagliano in their definitive study of metal urea complexes.[6] Invariably the group frequency approximation has been applied. These ideas have found their way into a recently published textbook.[7] It is pointed out in the first part of the argument that the formation of oxygen-to-metal bonds will be accompanied by a decreased bond order for the carbonyl group and that this will result in a shift of the carbonyl stretching vibration (amide I band) to lower frequencies. This is found to be the case when complexes are formed by simple aldehydes and ketones,[8] and similar arguments have been put forward for coordination through oxygen in ligands containing the M–O group where M = S, P, As, or N.[9]

The second part of the argument relies on simple valence bond considerations, as illustrated in eq 1, to



I II (1)

dictate that the formation of the oxygen-to-metal bond will be accompanied by an increase in the order of the amide C—N bond and that this will result in a shift of ν(C—N) to higher frequencies. The test of the mode of binding of amides is then straightforward: a shift of ν(C=O) to lower frequencies and of ν(C—N)

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[1] C. M. S. Yoder and J. J. Zuckerman, *Inorg. Chem.*, in press.

[2] G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960); R. J. G. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

[3] W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2144 (1960).

[4] M. Nardelli, *Gazz. Chim. Ital.*, **89**, 1616 (1959).

[5] The analogous thioacetamide complexes apparently bind likewise through the sulfur atom: L. Cavalca, M. Nardelli, and A. Braibanti, *ibid.*, **86**, 942 (1956).

[6] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

[7] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, pp 230, 231.

[8] L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

[9] (a) J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, **16**, 219 (1961); (b) F. A. Cotton, R. D. Barnes, E. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960); (c) S. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962); (d) J. V. Quagliano, T. Fujita, G. Franz, D. J. Phillips, J. A. Walmsby, and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 3770 (1961).

to higher frequencies would be taken as confirmation that the amide is bonding through its oxygen function (structure II). By analogous arguments, bonding through nitrogen should be accompanied by frequency shifts just the reverse of those cited above.[10]

By confining our discussion to aliphatic tertiary amides such as N,N-dimethylformamide (DMF), we can avoid the contributions which the NH in-plane and out-of-plane bending motions make to those modes which are normally regarded as the carbonyl and C—N stretching frequencies. We also avoid the difficulties due to changes of association in various condensed phases and are thus able to make use of data collected for various states of molecular aggregation.

TABLE I

N,N-DIMETHYLFORMAMIDE ABSORPTION BANDS[a]

A[b,c]	B[d,e]	C[e,f]	D[g]	E[h,i]	F (±2 cm^{-1})[j,k]
1661[l,m]	1675[l]	1674[l]	1681[l]	1650[l]	1685[l]
1389[n]	1393[o]	1396	1382[n]	1380[p]	1382[q]
1255[q]	r	1257[q]	1255[q]	1230[p]	1257[o]
1091[o]	1094[n]	1092[n]	1090[o]	1095[q]	1082[n]

[a] Units: cm^{-1}. [b] See ref 3. [c] Neat liquid or paraffin mull. [d] J. Archambault and R. Rivest, *Can. J. Chem.*, **38,** 1331 (1960). [e] Methylene chloride solution and neat liquid. [f] R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961). [g] In one paper [A. Clearfield and J. Malkiewich, *J. Inorg. Nucl. Chem.*, **25,** 237 (1963)] a shift of -10 cm^{-1} was ignored in favor of another band $+45$ cm^{-1} from the 1255-cm^{-1} band in the free amide. [h] R. C. Aggarwal and P. Singh, *Z. Anorg. Allgem. Chem.*, **332,** 103 (1964). [i] Neat liquid. [j] This work.[1] [k] CCl_4 solution. [l] Assigned to ν(C=O) by the original authors. [m] A value of 1675 cm^{-1} is listed for dilute methylene chloride solution. It is not clear from the paper in what phase the other values were derived. [n] Assigned to δ(C—H) by the original authors. [o] Assigned to ν(C′—N) by the original authors. [p] Values derived by us from published spectra. T. S. Piper and E. G. Rochow, *J. Am. Chem. Soc.*, **76,** 4318 (1954), did not yield sufficiently accurate values for useful comparison. [q] Assigned to ν(C—N) by the original authors. [r] Spectrum recorded in methylene chloride which obscures this region; not listed for spectrum of pure liquid.

TABLE II[a]

COMPLEXES OF DMF[b]

A[c]	B[d,e]			C[e,f]	D[g]	E[h,i]	F (±5 cm^{-1})[j,k]	
$BCl_3 \cdot DMF$	$TiCl_4 \cdot 2DMF$	$TiBr_4 \cdot DMF$	$TiI_4 \cdot n DMF$	$B_{10}H_{12} \cdot 2DMF$	$ZrCl_4 \cdot 2DMF$	$SnCl_4 \cdot 2DMF$	$SnCl_4 \cdot 2DMF$	$(C_6H_4O_2)_2Ge \cdot 2DMF$
1692[l]	1643	1642[m]	1653	1672	1658	1612	1650	1630
1333	1362	1340[m]	1367	1346	1367	1330	1360	1350
1248	n	1127	1123	1248	1330, 1245	1200	1240	1230
1136, 1058[o]	1118	1053	1096	1116, 1080[p]	1135	1125[q]	1125	1145, 1100

[a] Shifts in ν(C=O) on complexation are preferably referred to the vapor or *n*-hexane-solution values (1716 and 1696 cm^{-1}, respectively: L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55,** 14 (1959)). On this basis, studies of all DMF complexes are consistent for a fall in ν(C=O). [b] Units: cm^{-1}. [c] See ref 3. [d] See footnote *d*, Table I. [e] Methylene chloride solution and neat liquid. [f] See footnote *f*, Table I. [g] See footnote *g*, Table I. [h] See footnote *h*, Table I. [i] Neat liquid. [j] This work.[1] [k] Nujol mulls. [l] A value of 1686 cm^{-1} is listed for dilute methylene chloride solution. [m] Assigned to ν(C—N) by the original authors. [n] Spectrum recorded in methylene chloride which obscures this region; not listed for spectrum of pure liquid. [o] Both listed as weak. [p] Listed as medium and weak, respectively. [q] See footnote *p*, Table I.

In amides like DMF there are two types of C—N bond. Unfortunately no complete assignment of the infrared spectrum of DMF is available. It is clear from published studies on various formamides[11,12] that the force constant for the N-methyl bond in DMF should be smaller than the force constant for the C—N bond contiguous to the carbonyl. Thus ν(C—N) should be greater than ν(C′—N). Values for the four prominent absorption bands of DMF are listed with their previous assignments in Table I. The first has been consistently assigned to ν(C=O) and it is clear that another of the bands is associated with C—H deformation in the N-methyl group. On this basis three assignments are possible [the bands are given in order of decreasing frequency]: I: ν(C=O), δ(C—H), ν(C—N), ν(C′—N); II: ν(C=O), ν(C—N), δ(C—H), ν(C′—N); III: ν(C=O), ν(C—N), ν(C′—N), δ(C—H).

The present confused state of the literature is a result of a conflict between arguments for the shifts in ν(C—N) justified on theoretical grounds and the data from the spectra themselves. The assignment by some workers[13–16] of the last named band at 1082 cm^{-1} to ν(C—N) contiguous to the carbonyl *merely because it is found to shift to higher frequencies on coordination* must be mistaken.[17] We find in our complexes between DMF and compounds containing an element in group IV that shifts of ν(C=O) to lower frequencies are accompanied by shifts to lower frequencies of the two middle bands as well, one of which must be ν(C—N). This is also true in every case known to us[3,13–19] of DMF complexes with Lewis acids where the actual spectra or spectral data are published (see Table II).[19a]

Preliminary results with dimethylformamide-N^{15} give shifts of -7 cm^{-1} for a weak band at 1500 cm^{-1},

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(10) We can find no confirmed examples of this mode of bonding in the literature.

(11) S. I. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *J. Am. Chem. Soc.*, **72,** 3490 (1950); D. E. DeGraff and G. B. B. M. Sutherland, *J. Chem. Phys.*, **26,** 716 (1957).

(12) Microwave structural studies [C. C. Costain and J. M. Dowling, *ibid.*, **32,** 158 (1960)] show that the C–N band contiguous to the carbonyl is short and nmr spectroscopy of various N-substituted amides [A. J. R. Bourn, D. G. Gilles, and E. W. Randall, *Tetrahedron*, **22,** 1825 (1966), and references therein] confirm a high barrier to rotation in this bond.

(13) J. Archambault and R. Rivest, *Can. J. Chem.*, **36,** 1461 (1958).

(14) See footnote *d*, Table I.

(15) See footnote *h*, Table I.

(16) R. C. Aggarwal and P. Singh, *J. Inorg. Nucl. Chem.*, **27,** 2597 (1965).

(17) See footnote *g*, Table I.

(18) T. S. Piper and E. G. Rochow, *J. Am. Chem. Soc.*, **76,** 4318 (1954).

(19) See footnote *f*, Table I.

(19a) NOTE ADDED IN PROOF.—Our discussion also applies to the recent reports of R. C. Aggarwal and P. P. Singh [*J. Inorg. Nucl. Chem.*, **28,** 1655 (1966)], who assign ν(C–N) at 1095 cm^{-1} in free DMF and note a shift to 1126 and 1124 cm^{-1} on formation of $SnBr_4 \cdot 2DMF$ and $SnI_4 \cdot 2DMF$, respectively, and S. S. Krishnamurthy and S. Soundararajan [*ibid.*, **28,** 1689 (1966)], who assign ν(C–N) at 1094 cm^{-1} and note a shift to 1115 cm^{-1} on formation of $M(DMF)_4(NO_3)_3$ where M = La, Pr, Nd, Sm, or Y.

-13 cm^{-1} for the strong band at 1382 cm^{-1}, and -24 cm^{-1} for the medium band at 1257 cm^{-1}. The strong bands at 1685 and 1083 cm^{-1} were unaffected by the N^{15} substitution.[20] Occam's razor brings us to the conclusion that, if group frequency approximations must be applied, assignment III above is favored.

The data of Table II, however, in conjunction with the valence bond picture, constitute *prima facie* evidence for some coupling of ν(C—N) and ν(C′—N) with ν(C=O), *i.e.*, for the group frequency approximation being inadmissible here. Further work on other isotopomeric amide pairs is in progress.

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[20] M. R. Bramwell, E. W. Randall, and J. J. Zuckerman, unpublished results.

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The Differentiation between Unidentate and Bidentate Ligands Which Donate Three Electrons to a Metal Atom[1]

Sir:

During the last three years, work from this laboratory has resulted in the preparation and study of several new compounds of the general type $C_5H_5M(CO)_2T$ (M = Mo or W; T = neutral[2] ligand donating three electrons to a metal atom).[3] In compounds of this type it is possible for the three-electron donor ligand to be of several types[4] including the following: (a) unidentate occupying one coordination position of the metal atom through which the net donation of all three electrons occurs and (b) bidentate occupying two coordination positions of the metal atom. Donation of two of these three electrons occurs through one of the coordination positions and donation of the third electron occurs through the other coordination position. In a further comparative study of the infrared spectra of various $C_5H_5M(CO)_2T$ compounds in the metal carbonyl stretching region under high-resolution conditions[5,6] we have found an apparent means of differentiating between $C_5H_5M(CO)_2T$ compounds containing unidentate T ligands and those containing bidentate T ligands.[7]

Compounds of the type $C_5H_5M(CO)_2T$ (M = Mo or W) are expected to exhibit two metal carbonyl stretching frequencies. These predicted two frequencies are indeed observed (Table I) for those $C_5H_5M(CO)_2T$ compounds where T must clearly be monodentate (*i.e.*, the nitrosyl $C_5H_5Mo(CO)_2NO$). However, other $C_5H_5M(CO)_2T$ compounds such as the π-allyl derivative $C_5H_5Mo(CO)_2C_3H_5$ exhibit *four strong* metal carbonyl stretching frequencies (Table I). Since these four strong frequencies are observed in solution, they clearly cannot arise from solid-state effects. Since any possible single structure for $C_5H_5Mo(CO)_2C_3H_5$ can exhibit only two metal carbonyl stretching frequencies, the presence of four strong metal carbonyl frequencies indicates the presence of two different species in solution.[8]

TABLE I

METAL CARBONYL STRETCHING FREQUENCIES OF $TM(CO)_2C_5H_5$ COMPOUNDS (CM^{-1})[a]

A. Compounds Exhibiting Two Metal Carbonyl Stretching Frequencies	
$C_5H_5Mo(CO)_2NO$	2021 s, 1948 vs
$C_5H_5W(CO)_2NO$	2011 s, 1935 s
$C_6H_5N_2Mo(CO)_2C_5H_5$	2000 s, 1928 s
p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$	1997 s, 1925 s
p-$O_2NC_6H_4N_2Mo(CO)_2C_5H_5$	2010 s, 1942 s
π-$CH_3SCH_2Mo(CO)_2C_5H_5$	1952 s, 1869 s
π-$CH_3SCH_2W(CO)_2C_5H_5$	1941 s, 1856 s
π-$C_6H_5CH_2Mo(CO)_2C_5H_5$	1965 vs, 1873 m
B. Compounds Exhibiting Four Metal Carbonyl Stretching Frequencies	
π-$C_3H_5Mo(CO)_2C_5H_5$	1970 s, 1963 s, 1903 s, 1889 s
π-$C_7H_7Mo(CO)_2C_5H_5$	1968 s, 1962 s, 1915 s, 1900 s
π-$C_7H_7W(CO)_2C_5H_5$	1967 s, 1958 s, 1910 s, 1893 s

[a] Cyclohexane solution, Beckman IR-9 spectrometer; estimated error in frequencies $<\pm 2$ cm^{-1}.

If the π-allyl ligand in $C_5H_5Mo(CO)_2C_3H_5$ occupies two coordination positions, two isomers are clearly possible. X-Ray crystallographic studies[9] have shown

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[1] The author is indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-580-66.

[2] It is most convenient to regard such complexes as formed from neutral ligands and metal atoms. This is in accord with the formal structure of coordination chemistry presented by the author at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[3] For preparation of the compounds discussed in this paper, see the following references: (a) $C_5H_5M(CO)_2NO$ (M = Mo or W): T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955); (b) $RN_2Mo(CO)_2C_5H_5$: R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966); (c) π-$CH_3SCH_2M(CO)_2C_5H_5$ (M = Mo or W): R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965); (d) π-$C_3H_5Mo(CO)_2C_5H_5$: M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 899 (1963); (e) π-$C_7H_7M(CO)_2C_5H_5$ (M = Mo or W): R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964); R. B. King and A. Fronzaglia, *ibid.*, **5**, 1837 (1966); (f) π-$C_6H_5CH_2Mo(CO)_2C_5H_5$: R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[4] Other types of three-electron donor ligands include the following two possibilities: (a) tridentate ligands occupying three coordination positions of the metal atom with donation of one electron through each of these coordination positions of the metal atom and (b) bidentate ligands with three electrons donated through one of the coordination positions and zero electrons donated through the other coordination position.

[5] All of the spectra reported in Table I were recorded on a Beckman IR-9 spectrometer with grating optics and a scale expanded by a factor of 4. At this setting each millimeter of chart paper corresponded to about 1 cm^{-1} below 2000 cm^{-1} and to about 2 cm^{-1} above 2000 cm^{-1}. In order to obtain spectra with a minimum band width,[6] cyclohexane solutions were used in all cases.

[6] For a discussion of the band widths of metal carbonyl bands in various solvents see J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

[7] The $C_5H_5M(CO)_2T$ compounds shown to contain bidentate T ligands in this paper could also contain tridentate T ligands.

[8] The alternative possibility of Fermi resonance accounting for the doubling of the carbonyl frequencies appears unlikely since no evidence for it has been noted in any other alkyl or olefin derivatives of metal carbonyls.

[9] W. Baird and L. F. Dahl, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 27N.