Raman Spectra of Some Transition-metal Imido Complexes

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Raman and i.r. spectra of mono-organoimido (RN–) complexes of tungsten, rhenium, tantalum, and niobium and of bis(imido) complexes of tungsten have been measured, including ^{15}N substitution. Strong Raman bands near 1 350 (R = Ph), 1 295 (Me or Et), or 1 260 cm^{-1} (Bu^t) are attributed to symmetric stretching vibrations, while weaker Raman bands, 980—1 020 and 630—690 cm^{-1}, are assigned to asymmetric stretching and deformation modes, respectively, of the M–N–C linkage. The diagnostic application of Raman spectroscopy to imide chemistry is briefly discussed.

Although the i.r. spectra of a number of transition-metal imido complexes have been reported,[1] the assignment of the modes of the metal–imido ($M\equiv NR$) group remains in doubt. Thus, the metal–nitrogen stretch has been variously identified as a band or bands near 960[2] or 1 280 cm^{-1} [3,4] for tungsten, 930 cm^{-1} for vanadium,[5] 1 100 cm^{-1} for rhenium,[6] 1 200 cm^{-1} for osmium,[7,8] and 1 000—1 200 cm^{-1} for tantalum[9] imido complexes. A study of shifts produced by ^{15}N substitution in the i.r. spectra of rhenium[10] and of tantalum and niobium[11,12] complexes suggested that no clear distinction could be made between assignments of ν(M–N) and ν(N–C) for the bands near 990 and 1 340 cm^{-1}. In a recent paper on the i.r. spectra of normal and ^{15}N substituted $[V(\eta\text{-}C_5H_5)_2(NPh)]$ it was argued that a band at 934 cm^{-1} arises from ν(V–N) and one at 1 330 cm^{-1} from ν(N–C).[5]

The spectra of many imido complexes are complicated by vibrations of the co-ligands, and the i.r. bands assigned to imido vibrations are often not very strong or may be obscured by bands due to other ligands. We find that the Raman spectra of such complexes are much simpler in profile than those of the i.r. By the use of Raman together with i.r. spectroscopy of a number of mono- and bis-imido complexes, with ^{15}N substitution in some cases, we now attempt to clarify the assignment of M=NR modes. There is little previous information on the Raman spectra of imido complexes: there is a brief allusion to the spectra of $[W(NR)F_5]^-$ salts (R = Me, Et, or Bu^t)[13] and we have briefly reported the Raman spectra of some osmium oxoimido complexes.[8]

Results and Discussion

Our data on the Raman spectra of a number of mono- and bis-imido complexes over the range 200—1 700 cm^{-1} are given in the Table. Infrared spectra for some of the complexes have been reported before and our data in such cases are in close agreement with these. Although our solution data are poor, and restricted by low solubility, they indicate that the Raman bands at *ca.* 1 350 cm^{-1} are polarised while those near 680 cm^{-1} are depolarised. Measurements for $[\{W(NPh)Cl_4\}_2]$ and $[\{W(NPh)(OMe)_4\}_2]$ in tetrahydrofuran are given in the Table; others are for solids.

Assignment of Bands.—To minimise the complications caused by the presence of other polyatomic ligands, we first consider vibrational assignments for the pair of compounds $[\{W(NPh)Cl_4\}_2]$ (**1**) and $[\{W(NPh)(OMe)_4\}_2]$ (**2**). These have dimeric six-co-ordinate structures, bridged by chloro and methoxo groups respectively, with the phenylimido ligands in *trans*, diaxial positions of the dimer. The Raman spectrum of compound (**1**) is shown in the Figure.

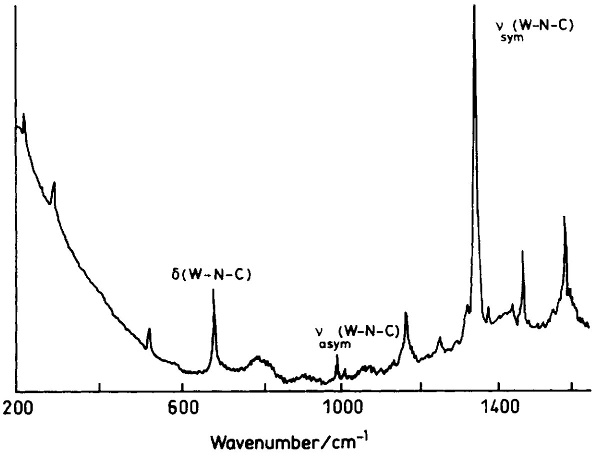

Figure. Raman spectrum of $[\{W(NPh)Cl_4\}_2]$ (**1**) as a spinning disc on KBr

Bands located near 680, 995, 1 010, 1 175, 1 350, 1 480, and 1 585 cm^{-1} are common to both compounds and are therefore likely to be associated with the phenylimido group. Comparison with the spectra of aryl organometallic compounds[14] leads to the assignment of the bands at 995, 1 175, 1 480, and 1 585 cm^{-1} to ring stretching modes of the phenyl substituent. Of the remaining bands, only one differs markedly in frequency between the two compounds, being located at 1 349 cm^{-1} for (**1**) and at 1 368 cm^{-1} for (**2**). This band, which is the most intense Raman feature, although an obvious candidate for the ν(W–N) mode, probably arises from the W–N–C linkage as a whole.

Assignment of this strong Raman band to symmetric stretching of the W–N–C linkage is supported by its being polarised for the complexes in solution, and by the result of ^{15}N labelling of compound (**1**) which lowers the wavenumber by 17 cm^{-1}. The much weaker band at 998 cm^{-1} shifts to 983 cm^{-1} on ^{15}N substitution and that at 683 cm^{-1}, which is probably due to the W–N–C bending mode, shifts to 678 cm^{-1}. A drop in wavenumber of 15—20 cm^{-1} is clearly not that of a simple ν(M–N) mode (for which a shift of *ca.* 40 cm^{-1} might be expected). Previous assignments have attempted to separate M–N and N–C stretching frequencies[2–9] using mainly i.r. data, but the additional evidence from Raman spectra favours the view[10–12] that no clear distinction can be made and that bands in the 930—1 020 and 1 330—1 370 cm^{-1} ranges for phenyl-

Table. Raman spectra (cm^{-1}) of transition-metal imido compounds

Compound	ν_{sym}(M–N–C)	ν_{asym}(M–N–C)	δ(M–N–C)	ν(phenyl ring)	ν(M–Cl)	Other bands
Monoimido						
$[\{W(NPh)Cl_4\}_2]$*	1 349vs, p	998w, dp	683m, dp	995w, 1 173w, 1 478m, dp, 1 583m, p	220m, 286w	540w, 844w, 1 016w, 1 270w
$[\{W(^{15}NPh)Cl_4\}_2]$	1 332vs	983w	678m	995w, 1 172w, 1 477m, 1 581m	218m, 286w	540w, 844w, 1 016w, 1 270w
$[NMe_4][W(NPh)Cl_5]$	1 351vs	962w	677m	999w, 1 170w, 1 490m, 1 580m	250m, 290w	325w, 370w, 580w, 1 005w, 1 040w
$[W(NPh)Cl_4(py)]$	1 354vs	1 010m	678m	996w, 1 166w, 1 473m, 1 580m	240m, 285m	317w, 363m, 638w, 805w, 1 018w
$[\{W(NPh)(OMe)_4\}_2]$*	1 368vs, p	1 012m, dp	680m, dp	994w, p, 1 175m, dp 1 488s, dp, 1 586s, p	—	565w, p, 625w, dp 1 033w, p, 1 286w, dp
$[\{W(NPh)(OEt)_4\}_2]$	1 363vs	1 007m	674m	990w, 1 169m, 1 485s, 1 585s	—	476w, 525m, 550w, 1 028w
$[\{W(NPh)(OEt)_2Cl_2\}_2]$	1 356vs	1 010w	677w	995w, 1 170w, 1 479m, 1 583s	210m, 280m	325m, 560w, 666w, 1 020w
$[\{W(NPh)(OEt)Cl_3\}_2]$	1 360vs	1 000m	677m	992w, 1 172m, 1 484s, 1 582s	215w, 285w	338s, 566w, 911w, 1 031w, 1 275w
$[Re(NPh)Cl_3(PPh_3)_2]$	1 329m, 1 345vs	1 014m	680m	1 170m, 1 475s, 1 581s	213w, 281m	530w, 622w, 1 004m, 1 028w, 1 130w
$[Re(^{15}NPh)Cl_3(PPh_3)_2]$	1 316s, 1 326vs	1 008m	678m	1 170m, 1 473m, 1 580s	213w, 281m	530w, 622w, 1 002w, 1 028w, 1 130w
$[\{Ta(NEt)(NHEt)Cl_2(NH_2Et)\}_2]$	1 294s	995w	683w	— —	217m, 355m	472m, 615m, 883w, 1 052m, 1 452m
$[\{Nb(NBu^t)Cl_3(NH_2Bu^t)\}_2]$	1 236m	998w	—	— —	281m	347m, 1 146m, 1 452w
Bis(imido)						
$[W(NPh)_2Cl_2(bipy)]$	1 307s, 1 339vs	987s	658m	1 152m, 1 463s, 1 562s	216m, 259m	620w, 1 009m, 1 089w
$[W(NPh)_2Cl_2(phen)]$	1 300s, 1 341vs	987s	663m	1 150m, 1 463s, 1 564s	217m, 252w	530w, 606w, 718m, 1 038w, 1 406w, 1 436w
$[W(NPh)_2Cl_2(NH_2Ph)_2]$	1 319m, 1 334s	983w	643s	1 154m, 1 463m, 1 565s	240m, 275w	472m, 593m, 686w, 1 210m, 1 246m
$[\{W(NPh)(NBu^t)Cl_2(NH_2Bu^t)\}_2]$	1 263s, 1 357m	999s	678m	1 152w, 1 484m, 1 589s	262w, 282w	404w, 527w, 922w, 1 033w, 1 152w, 1 235m
$[\{W(NMe)(NBu^t)Cl_2(NH_2Bu^t)\}_2]$	1 253s, 1 296w	995m	636s	— —	250w, 287m	389m, 606m, 808m, 1 150s

* Data on solutions in tetrahydrofuran: all other data on solids. p = Polarised, dp = depolarised.

imido compounds should be used to interpret questions of bonding of this ligand. The present series of tungsten compounds exhibit frequencies at the upper end of these ranges which indicates larger M–N and N–C force constants and stronger bonding than in some compounds of lighter transition metals, *e.g.* $[V(\eta\text{-}C_5H_5)_2(NPh)]$.[5]

Several bis(organoimido) compounds have also been examined and here the spectra exhibit pairs of bands, as expected since they are known to contain *cis*-imido ligands.[15] For example, the single strong band at 1 349 cm^{-1} of compound (**1**) and at 1 354 cm^{-1} of $[W(NPh)Cl_4(py)]$ (py = pyridine) is replaced by 1 339 and 1 307 cm^{-1} in the Raman spectrum of $[W(NPh)_2Cl_2(bipy)]$ (bipy = 2,2′-bipyridyl). The relative intensities suggest that these arise from in-phase and out-of-phase stretching modes, respectively, of the C–N–W–N–C skeleton. The frequency of the phenyl mode near 1 600 cm^{-1} is known to be indicative of ring conjugation,[16] and it is therefore noteworthy that there is a change from about 1 585 cm^{-1} for mono(phenylimido) complexes of tungsten to about 1 565 cm^{-1} for the bis(phenylimido) species.

Several alkylimido complexes are included in the present study. Our assignments in the Table for ν(M–N–C) near 1 295 cm^{-1} for the MeN and EtN ligands and 1 236—1 263 cm^{-1} for Bu^{t}N complexes receive support from the similar assignments for $[W(NR)F_5]^-$ in which the dependence on R is as follows: R = Me, 1 332; Et, 1 314; and Bu^t, 1 286 cm^{-1}.[13]

Diagnostic Use of Raman Spectroscopy.—In general metal–nitrido complexes (containing the M$\equiv$N unit with a terminal nitride ligand) are easily recognisable in their vibrational spectra by the intensity of both the Raman and coincident i.r. stretching mode, ν(M$\equiv$N), which normally occurs in the 1 050—1 150 cm^{-1} range.[17] The i.r. spectra of imido complexes, however, have no such distinguishing feature. We have shown in this work that the high intensity of the band which we assign to symmetric stretching of the M$\equiv$NR group near 1 350 cm^{-1} for phenylimido complexes and near 1 230—1 300 cm^{-1} for alkylimido complexes in the Raman spectra can indeed be taken as indicating the presence of a co-ordinated imido ligand.

Experimental

The compound $[\{W(NPh)Cl_4\}_2]$ was prepared from $[(WOCl_4)_n]$ and phenyl isocyanate[18] and $[\{W(^{15}NPh)Cl_4\}_2]$ by reaction of $[(WOCl_4)_n]$ with Ph^{15}NSO in benzene;[19] $[NMe_4][W(NPh)Cl_5]$ and $[W(NPh)Cl_4(py)]$ were prepared by reaction of NMe$_4$Cl or pyridine with $[\{W(NPh)Cl_4\}_2]$,[20,21] $[\{W(NPh)(OR)_{4-x}Cl_x\}_2]$ by reaction of the appropriate alcohol with $[\{W(NPh)Cl_4\}_2]$ in the presence of a t-butylamine,[22,23] $[Re(NPh)Cl_3(PPh_3)_2]$ and $[Re(^{15}NPh)Cl_3(PPh_3)_2]$ from $[Re(O)Cl_3(PPh_3)_2]$ and PhNH$_2$ or Ph^{15}NH$_2$,[24] $[\{Ta(NEt)(NHEt)Cl_2(NH_2Et)\}_2]$ from TaCl$_5$ and ethylamine,[25] and $[\{Nb(NBu^t)Cl_3(NH_2Bu^t)\}_2]$ from NbCl$_5$ and

$SiMe_3(NHBu^t)$.[25] The bis(organoimido) complexes $[\{W(NR)(NR')Cl_2(NH_2R')\}_2]$ were prepared by reaction of the mono-organoimido complexes $[\{W(NR)Cl_4\}_2]$ (R = Ph or Me) with the silylamines $SiMe_3(NHR')$ (R′ = Ph or Bu^t)[26] and the $[W(NPh)_2Cl_2(L)]$ complexes [L = 2,2′-bipyridyl or 1,10-phenanthroline (phen)] from $[\{W(NPh)_2Cl_2(NH_2Ph)\}_2]$ and L.[27]

Raman spectra were measured using a Spex Ramalog 5 instrument with a krypton-ion laser (excitation at 530.8, 568.2, or 614.7 nm) or a Jasco R300 spectrometer with argon-ion laser (excitation at 488.0 or 514.5 nm) with samples in capillary tubes or as spinning discs in a KBr base. Polarisation measurements were performed on solutions of $[\{W(NPh)Cl_4\}_2]$ and $[\{W(NPh)(OMe)_4\}_2]$ in tetrahydrofuran. Infrared spectra were measured on Perkin-Elmer 597 or 683 instruments as liquid paraffin mulls between CsI plates.

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