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Low-Energy Vibrational Spectra of Some Imidazole Complexes

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Vibrational spectra in the range 70–500 cm^{-1} are reported for the compounds ML_6X_2 (L = imidazole; M = Mn and X = Cl, Br, I, NCS; M = Co, Ni and X = Cl, Br, I, NO_3; M = Cu and X = I, NO_3; M = Zn and X = Cl, NO_3), ML_4X_2 (M = Mn and X = Cl; M = Ni and X = Cl, Br, I; M = Cu and X = Cl, Br, I, NO_3; M = Zn and X = NO_3), $MnL_4X_2 \cdot 2H_2O$ (X = Br, I), $NiL_4X_2 \cdot 2H_2O$ (X = Cl, Br), ML_2X_2 (M = Mn and X = Cl, Br; M = Co, Zn and X = Cl, Br, I, NO_3; M = Cu and X = NO_3), and MLX_2 (M = Mn and X = Cl; M = Ni and X = Cl, Br). Where possible, these are related to the stereochemistries of the complexes as determined by electronic spectra, esr, and magnetic susceptibility measurements.

Introduction

As part of a program to determine the low-energy vibrational spectra of complexes with biologically important ligands, we report here results for some complexes of imidazole (=L), a ring system which occurs in numerous more complicated biologically significant systems. During the preparation of this paper, partial vibrational spectra (infrared, 450–180 cm^{-1}) were reported[1] for a few of the compounds we have studied. We include here our own results for these cases for completeness.

Experimental Section

Unless stated otherwise, the compounds were vacuum dried over phosphorus pentoxide. Analytical results (Microanalytical Laboratory, Imperial College) for all of the compounds were good.

MnL_6X_2 (X = Cl, Br, I, NCS).—An excess of imidazole in warm ethanol (acetone for the iodide) was added to a solution of the appropriate metal salt in the same solvent. The precipitated compounds were washed with ether and dried (the thiocyanate initially formed as an oil). The iodide and thiocyanate were recrystallized from benzene.

MnL_4Cl_2 and $MnL_4X_2 \cdot 2H_2O$ (X = Br, I).—The anhydrous compounds were obtained from the calculated quantities of imidazole and manganese(II) halide in warm ethanol (X = Cl) or acetone (X = Br, I) but the bromide and iodide rapidly hydrated in air.

MnL_2X_2 (X = Cl, NCS).—Imidazole and the manganese(II) salt were mixed in a 2:1 mole ratio in hot ethanol. The thiocyanate precipitated as green crystals, but the chloride was obtained only on adding ether.

MnL_2X_2 (X = Br, I).—The corresponding MnL_6X_2 compounds were heated *in vacuo* at 100° for several days. The pale yellow iodide was very hygroscopic and rapidly turned brown in the air. Decomposition was slower (several weeks) in dry air.

$MnLCl_2$.—This was prepared from a 1:1 mixture of imidazole and manganese(II) chloride in warm ethanol.

ML_6X_2 (M = Co, Ni; X = Cl, Br, I, NO_3).—These were obtained essentially as described by Eilbeck, *et al.*,[2] but we found that crystallization occurred without the addition of ether.

CoL_2X_2 (X = Cl, Br, I, NO_3).—Solutions of imidazole and the hydrated cobalt salt in a 1.9:1 mole ratio in ethanol or nitromethane (X = NO_3) were evaporated down to small bulk, a little dichloromethane was added, and the solutions were stored at 0° for several days. The crystals which formed (from an oil in the case of the nitrate) were filtered off, washed with anhydrous ether, and dried. The dark red nitrate was very hygroscopic.

$NiL_4X_2 \cdot 2H_2O$ (X = Cl, Br, I).—Pale blue crystals were obtained from concentrated ethanolic solutions of imidazole and the hydrated nickel halide in a 4:1 mole ratio at room temperature. The compounds were filtered off, washed with a little ice-cold acetone, and air dried. The iodide spontaneously lost water to form yellow-orange tetrakis(imidazole)nickel(II) iodide.

NiL_4X_2 (X = Cl, Br).—These were obtained on heating the corresponding dihydrates at 120° for 24 hr.

$NiL_4X_2 \cdot 2D_2O$ (X = Cl, Br).—The anhydrous compounds were placed in an atmosphere of D_2O for 5 hr.

$NiLX_2$ (X = Cl, Br).—Equimolar mixtures of imidazole and the nickel halide in ethanol were evaporated to dryness. The pale yellow solids were washed with acetone and ethanol and dried at 120°.

CuL_4X_2 (X = Cl, Br, NO_3).—Dark blue-purple crystals separated on mixing imidazole and the appropriate, hydrated copper salt in a 4.4:1 mole ratio in ethanol. The products were washed with acetone and ether.

CuL_4I_2.—The calculated quantity of KI in hot ethanol was added to a hot ethanolic solution of imidazole and cupric perchlorate (6:1 mole ratio) and the precipitate of potassium perchlorate was filtered off. The dark green-blue solution was evaporated somewhat and allowed to cool when dark purple crystals separated. These were filtered off and washed with ether.

$CuL_4I_2 \cdot 2L$.—CuL_4I_2 was dissolved in the minimum quantity of ethanol containing a 3:1 molar excess of imidazole. Dark blue crystals formed on storing at 0° overnight. These were collected as above.

$CuL_4(NO_3)_2 \cdot 2L$.—A 3:1 molar excess of imidazole was added to a suspension of $CuL_4(NO_3)_2$ in nitromethane. A little dichloromethane was added to the resulting blue solution, and, on storing at 0° overnight, dark blue crystals were formed, which were collected and dried.

$CuL_2(NO_3)_2$.—On mixing hot solutions of imidazole and hydrated cupric nitrate in 2,2-dimethoxypropane in a 2:1 mole ratio, a blue oil was formed, which crystallized on standing overnight at room temperature. The hygroscopic solid was washed with 2,2-dimethoxypropane and then ether.

ZnL_6X_2 (X = Cl, NO_3).—An acetone solution of imidazole was added in a 6.6:1 mole ratio to an acetone suspension of the appropriate zinc salt. The resulting solution was evaporated down to small bulk and a small volume of dichloromethane was added. The solution was stored at 0° until the oil which initially formed had crystallized (*ca.* 4 days). The chloride was hygroscopic.

$ZnL_4(NO_3)_2$.—A hot ethanolic solution of imidazole was added in a 4:1 mole ratio to one of zinc nitrate hexahydrate. The white complex was obtained after concentration and cooling.

ZnL_2X_2 (X = Cl, Br, I, NO_3).—These were prepared similarly to ZnL_6X_2, using the calculated quantity of imidazole with nitromethane as solvent. The nitrate was hygroscopic.

Physical Measurements.—Grubb-Parsons DM4 and GM3 spectrometers were used to obtain the low-frequency infrared spectra, with the samples as Vaseline mulls between polythene

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(1) W. J. Eilbeck, F. Holmes, C. E. Taylor, and A. E. Underhill, *J. Chem. Soc., A*, 128 (1968).

(2) W. J. Eilbeck, F. Holmes, and A. E. Underhill, *ibid.*, 757 (1967).

plates. Raman spectra were obtained with a Cary Model 81 He–Ne laser instrument. Samples were finely powdered and pressed into small glass tubes. Some of the CoL_6X_2 compounds tended to decompose in the laser beam at full power, and for these it was necessary to attenuate the beam and to record spectra several times to check reproducibility. Even so, it is possible that some weak bands are due to decomposition products.

Diffuse reflectance spectra were obtained on a Beckman DK2A spectrometer. A conventional Gouy balance was used for the magnetic measurements, and the esr spectra were obtained using a Varian V-4502-15 X-band spectrometer.

Results and Discussion

Infrared and Raman spectra of the compounds were obtained over the range 70–400 cm^{-1}. Studies were restricted to the solid state because of poor solubility in solvents which did not cause decomposition, and no polarization results could be obtained for the Raman spectra. The compounds are weak Raman scatterers, and it was necessary to use high sensitivity to observe the bands. Weak bands below 150 cm^{-1} were therefore seen only as shoulders on the side of the exciting line. For blue compounds no Raman spectra were observed.

The vibrational bands of imidazole below 400 cm^{-1} are given in Table I, with the results of previous workers.[3–5] These bands have been ascribed[3–5] to lattice modes involving N···H–N hydrogen bonds. The spectra of the metal complexes will be discussed for each of the main stereochemical arrangements in turn.

TABLE I

VIBRATIONAL SPECTRA (CM^{-1}) OF IMIDAZOLE BELOW 400 CM^{-1}

Spectrum	Peaks	Ref
Raman	149 s, 89 m, 77 m	This work[a]
	125, 96, 75, 45	3
Ir	179 w, 143 s, 115–105 w, vbr, 88 m	This work[a]
	140 s, 104 m, br, 63 vw	4
	177 mw, 141 s, 87 mw	5

[a] Studied down to 70 cm^{-1} only.

TABLE II

VIBRATIONAL BANDS (CM^{-1}) AT 70–350 CM^{-1} FOR THE COMPOUNDS ML_6X_2 (L = IMIDAZOLE)

	Spectrum[a]	ν_1	ν_2	ν_3	(ν_3 or ν_4)[b]	Other bands
MnL_6Cl_2	Ir			205 s	182 s	230 sh, 152 s, 122 w, 108 vw
	R	169 s	131 s			106 sh
MnL_6Br_2	Ir			205 s	170 vs	143 s, 112 w, br, 82 vw
	R	167 m	122 sh			105 sh
MnL_6I_2	Ir			212 s	178 vs	152 m, 107 m
$MnL_6(NCS)_2$	Ir			205 vs	176 ms	162 m
	R	179 s	166 sh			100 sh
CoL_6Cl_2	Ir			236 s, 200 m	176 ms	145 ms, 133 m, 114 w, 101 w
	R	188 m	163 w			
CoL_6Br_2	Ir			236 s, br, 197 m	174 s	110 ms
	R	192 m	159 mw			113 m
CoL_6I_2	Ir			238 s, br, 197 m	173 m	100 m, br
	R	189 s	156 m			103 ms
$CoL_6(NO_3)_2$	Ir			239 s, 199 m	175 s	127 s, br
	R	189 ms	162 w			140 sh, 112 sh
NiL_6Cl_2	Ir			258 s	189 m	210 vw, 148 m, 135 sh
	R	210 m	171 w			
NiL_6Br_2	Ir			259 s	186 m	111 s, br
	R	210 s	166 w, br			
NiL_6I_2	Ir			262 s	184 ms	107 mw
	R	207 s	164 w, br			
$NiL_6(NO_3)_2$	Ir			262 s	188 m	212 vw, 130 s
	R	208 m	175 sh			
ZnL_6Cl_2	Ir			199 s	171 s	308 w, br, 154 s, br, 133 s, br, 110 ms
	R	185 s	153 m, br			203 w, 133 s, 102 m
$ZnL_6(NO_3)_2$	Ir			201 vs	163 s	126 s
	R	192 s	154 sh			113 s

[a] Ir, infrared; R, Raman. [b] See text for discussion of this assignment.

TABLE III

VIBRATIONAL FREQUENCIES (CM^{-1}) OF THE NITRATE GROUP IN THE COMPLEXES

Compound	Spectrum	ν_1[a]	ν_2	ν_3	ν_4[b]
$CoL_6(NO_3)_2$	Ir	...	824 m	1372 s	710 m
	R	1045 s	...	...	714 m
$NiL_6(NO_3)_2$	Ir	...	823 m	1375 s	710 m
	R	1045 s	...	...	712 m
$ZnL_6(NO_3)_2$	Ir	...	824 m	1372 s	711 m
	R	1043 s	...	...	712 m
$CuL_4(NO_3)_2$	Ir	1047 m	823 m	1371 s, br, 1340 s	708 w
$CuL_4(NO_3)_2\cdot 2L$	Ir	1043 m	824 m	1370 s, br, 1337 s	703 w
$ZnL_4(NO_3)_2$	Ir	1033 s	811 m	1455 s, 1400 s, 1312 s	717 m, 703 w
	R	1036 s	...	...	720 m, 707 m
$CoL_2(NO_3)_2$	Ir	1034 s, 1005 s	806 s	1475 s, br, 1320 s, 1273 s	703 w
$CuL_2(NO_3)_2$	Ir	1021 s	811 m, 808 m	1456 s, br, 1418 s, br, 1290 s, br	
$ZnL_2(NO_3)_2$	Ir	1037 s, 1008 s	809 s	1473 s, br, 1332 s, 1278 s	708 w
	R	1039 s, 1009 s	...	...	723 m, 710 m

[a] Free-ion notation. [b] Strong ligand band near 725 cm^{-1}.

Octahedral Complexes, ML_6X_2.—The compound $ZnL_6Cl_2\cdot 4H_2O$ contains distorted octahedral ZnL_6^{2+} ions with the imidazoles coordinated through the tertiary nitrogen.[6] This cation is assumed to be present in the anhydrous compound studied here and, from the similarity in the vibrational spectra (Table II), also in the analogous nitrate. The presence of ionic nitrate in $ZnL_6(NO_3)_2$ is also shown by the vibrational bands of this anion (Table III).

Essentially octahedral ML_6^{2+} ions are also present in the 6:1 complexes of cobalt(II) and nickel(II),[2] and from the similarity of their low-energy vibrational spectra this also appears to be the case for the manganese(II) analogs.

However, the CuL_6X_2 stoichiometry of the cupric nitrate and iodide complexes is unusual. In the former, the asymmetric stretch (ν_3) of the anion is split into two components (Table III) almost identical in position with those found for $CuL_4(NO_3)_2$. The esr spectrum of $CuL_6(NO_3)_2$ is anisotropic and shows hyperfine splitting ($g_{||}$ = 2.35, $g_{\perp}$ = 2.07, $|A|$ = 0.019 cm^{-1}; *cf.* CuL_4-

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(3) H. Zimmerman, *Z. Elektrochem.*, **65**, 821 (1961).

(4) C. Perchard, A-M. Bellocq, and A. Novak, *J. Chim. Phys.*, **62**, 1344 (1965).

(5) M. Cordes de N.D. and J. L. Walter, *Spectrochim. Acta*, **A27**, 237 (1968).

(6) C. Sandmark, *Acta Chem. Scand.*, **21**, 993 (1967).

$(NO_3)_2$ in frozen solution:[7] $g_{\|} = 2.267$, $g_{\perp} = 2.063$, $|A| = 0.018$ cm^{-1}). The esr spectrum of CuL_6I_2 was also anisotropic but, because of exchange broadening, $g_{\|}$ and $g_{\perp}$ could not be satisfactorily assigned. The low-frequency infrared spectra differed markedly from the other ML_6X_2 compounds and were similar to the 4:1 copper complexes. It seems likely that these compounds are of the type $CuL_4X_2 \cdot 2L$, as suggested[8] for $Cu(py)_4(NO_3)_2 \cdot 2py$. Accordingly their vibrational spectra are included with those of the other tetragonally distorted octahedral complexes (Table IV).

TABLE IV

VIBRATIONAL BANDS (CM^{-1}) AT 70–400 CM^{-1} FOR SOME IMIDAZOLE COMPLEXES WITH DISTORTED OCTAHEDRAL, POLYMERIC OCTAHEDRAL, AND SQUARE STEREOCHEMISTRIES

		Distorted Octahedral
MnL_4Cl_2	Ir	235 sh, 208 sh, 175 s, vbr
	R	144 sh
$MnL_4Br_2 \cdot 2H_2O$	Ir	299 w, 227 s, 185 s, 160 s, br, 120 sh, 105 ms
	R	286 w, 274 sh, 222 w, 180 s, 114 sh, 100 sh
$MnL_4I_2 \cdot 2H_2O$	Ir	300 w, 218 s, 202 s, 182 vs, 153 vs, br, 122 mw, 96 s
	R	287 w, 178 ms, 142 sh, 120 sh, 92 sh
NiL_4Cl_2	Ir	257 s, 232 s, 150–175 m, br
$[NiL_4(H_2O)_2]Cl_2$	Ir	270 m, 250 sh, 241 s, 233 sh, 205 w, 170 sh, 147 s, br
	R	224 w, 178 w, br
$[NiL_4(D_2O)_2]Cl_2$	Ir	268 m, 245 sh, 238 s, 226 sh, 204 w, 169 m, 147 s, br
	R	223 mw, 180 mw
$[NiL_4(H_2O)_2]Br_2$	Ir	263 s, 248 m, 238 s, 227 sh, 195 m, 169 w, 158 w, 114 ms
	R	221 w, 179 w, br
$[NiL_4(D_2O)_2]Br_2$	Ir	261 m, 243 m, 234 ms, 220 sh, 193 ms, 168 m, 155 w, 113 s
	R	220 w, 175 vw, br
CuL_4Cl_2	Ir	287 ms, 254 w, 225 m, 176 sh, 160 s, 126 s, 112 m
CuL_4Br_2	Ir	287 ms, 254 w, 224 w, br, 170 m, 152 w, 125 s, br
CuL_4I_2	Ir	287 s, 251 ms, 223 w, br, 158 w, br, 114 vs
$CuL_4I_2 \cdot 2L$	Ir	282 s, 255 w, 223 mw, 176 m, 158 s, 126 ms, 114 sh
$CuL_4(NO_3)_2$	Ir	290 s, 257 w, 225 w, 168 m, 145 ms, br, 118 s
$CuL_4(NO_3)_2 \cdot 2L$	Ir	296 m, 267 ms, 241 s, 218 s, 155 ms, br, 130 ms, br
$ZnL_4(NO_3)_2$	Ir	271 ms, 202 m, 160 vs, 120 mw, 105 w
	R	268 w, br, 219 sh, 204 mw, 177 m, 147 s, 90 sh
		Polymeric Octahedral
MnL_2Cl_2	Ir	250 sh, 214 s, 194 s, 159 m, 135 m, 105 mw
MnL_2Br_2	Ir	250 m, 193 s, 176 s, 161 ms, 136 m, 100 w
MnL_2I_2[a]	Ir	200 sh, 182 s, 155 vs, 126 w, 100 m
$MnL_2(NCS)_2$	Ir	244 s, br, 170 s, br, 128 s, br
	R	209 s, 147 s, 126 m, 105 sh
$MnLCl_2$	Ir	250 s, 238 vs, 178 vs, 148 s, 118 s
$NiLCl_2$	Ir	276 m, 255 m, 210 s, 181 s, 150 m
	R	278 mw, 243 w, 210 w, 195 ms, 182 w
$NiLBr_2$	Ir	259 m, 239 s, 220 m, 194 s, 179 s, 155 s, 139 m
	R	265 w, 226 w, 198 m, 180 w, 156 m
		Square
NiL_4Br_2	Ir	393 m, 329 m, 130 s, 98 ms
	R	289 w, 239 mw, 183 ms, 113 ms
NiL_4I_2	Ir	389 m, 326 mw, 124 mw, 91 mw
	R	288 w, 236 m, 179 m

[a] Unstable compound; see text.

The low-energy vibrational bands for the other ML_6X_2 compounds are given in Table II. Although the electronic spectra of the nickel and cobalt complexes gave no indication of distortion of the cations from O_h symmetry,[2] assignment of the vibrational spectra using this point group for the MN_6 units is not straightforward. The Raman bands at 167–210 and 122–175 cm^{-1} may be reasonably assigned as ν_1 (A_{1g}) and ν_2 (E_g), respectively. It is also very likely that the strong infrared band in the 200–262-cm^{-1} region is ν_3 (F_{1u}). In the cobalt complexes there is, as well as a strong band at 237 ± 2 cm^{-1}, a weaker band at $\sim$200 cm^{-1}. This was tentatively assigned by Eilbeck, *et al.*,[1] as δ(NMN), ν_4 (F_{1u}), but we prefer to assign it as a component of ν_3, owing to a departure from O_h symmetry.

The difficulty arises with the assignment of the medium-to-strong infrared band at 163–189 cm^{-1}. Its relative constancy for a given metal ion on changing the anion suggests that it is not a lattice mode. It is tempting to assign it as ν_4, but its proximity to ν_3 casts some doubt on this (compare: ν_3 at 330 cm^{-1} and ν_4 at 215 cm^{-1} for $Ni(NH_3)_6Cl_2$[9]), as does an order $\nu_4 > \nu_2$. Alternatively this band could be a component of ν_3.

The bands below 150 cm^{-1} were anion dependent and are attributed to lattice modes. Two of the nickel compounds have a very weak infrared band near 210 cm^{-1}. This is close in energy to ν_1, the M–L symmetric stretch, and it seems likely that this mode is activated in the infrared spectrum by a departure from O_h symmetry.

Tetragonally Distorted Octahedral Complexes.—As the precise structures of these compounds are unknown, detailed band assignments will not be attempted. In most cases the spectra (Table IV) are more complicated than would be expected on the assumption of D_{4h} symmetry for a *trans*-ML_4X_2 unit.

The infrared spectra of the copper compounds CuL_4X_2 have three anion-independent bands in the 200–300-cm^{-1} region. These are probably the three ν(M–L) bands expected for a distorted CuL_4 plane. The energies of the electronic bands of the complexes CuL_4X_2 alter on varying X (Table V) suggesting that the anions are coordinated, but ν(Cu–X) bands, expected below 200 cm^{-1}, could not be identified.

The vibrational spectra of the other anhydrous 4:1 complexes have bands at frequencies similar to those assigned as ν_1, ν_2, and ν_3 for the ML_6^{2+} cations, and these may be ascribed to modes with predominantly M–L stretching character. Many of the compounds show extra bands above 200 cm^{-1}. In some cases these may be assigned as ν(M–X) bands. For example, the strong 232-cm^{-1} band in the infrared spectrum of NiL_4Cl_2 is probably ν(Ni–Cl) (compare: 246 cm^{-1} in $Ni(py)_4Cl_2$[10]), and the 271-cm^{-1} band of $ZnL_4(NO_3)_2$ may be assigned as ν(Zn–ONO_2). The infrared spectra of the hydrates are more complicated.

The electronic spectrum of the anhydrous nickel chloride complex is quite different from that of its hydrate (Table V). The degree of axial distortion in the former is considerable, and the magnitude of the tetragonal splitting parameters[11] ($Ds \sim 100$ cm^{-1}, $Dt \sim 490$ cm^{-1}) is unusual in that Dt is much larger than Ds. The most likely reasons for this are either that there is a large

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[7] B. G. Malmström and T. Vänngård, *J. Mol. Biol.*, **2**, 118 (1960).

[8] R. V. Biagetti, W. G. Boltjer, and H. M. Haendler, *Inorg. Chem.*, **5**, 379 (1966).

[9] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

[10] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

[11] W. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

TABLE V

DIFFUSE REFLECTANCE SPECTRA AND ROOM-TEMPERATURE MAGNETIC MOMENTS OF SOME IMIDAZOLE COMPLEXES

Complex	Frequency, kK	μ_{eff}, BM
CuL_4Cl_2	16.9	1.84
CuL_4Br_2	~14.8 sh, 17.4	1.84
CuL_4I_2	~14.5 sh, 18.2	1.81
$CuL_4(NO_3)_2$	~16.7 sh, 18.4	1.75
$CuL_4I_2 \cdot 2L$	16.8 br	...
$CuL_4(NO_3)_2 \cdot 2L$	15.9	1.84
$CuL_2(NO_3)_2$	13.5, 15.6 sh	1.86
NiL_4Cl_2	6.45, 10.7, 14.7, 17.5 w, sh, 24.8	3.14[a]
$NiL_4Cl_2 \cdot 2H_2O$[b]	9.1, 11.0, ~13.8 sh, 16.8, 27.25	3.17
$NiL_4Br_2 \cdot 2H_2O$[b]	9.1, 10.9, ~13.7 sh, 16.7, 27.25	3.18
NiL_4Br_2	21.7	Diamag
NiL_4I_2	21.1	Diamag
$NiLCl_2$	~6.3 sh, 7.7, 12.0, 12.95, ~18.7 sh, 22.1	3.44
$NiLBr_2$	~5.9 sh, 7.3, ~11.3 sh, 12.3, ~18.0 sh, ~18.7 sh, 21.4	3.17
$CoL_2(NO_3)_2$	6.17, 7.70, 9.1, 11.1 sh, 18.4	4.42
CoL_2Cl_2	4.85, 6.38, 7.50, 9.15, 16.1, 17.4, *d*	4.66
CoL_2Br_2	6.15, 6.90, 8.70, 15.0, 16.1, 17.2, *d*	4.63
CoL_2I_2	6.60,[c] 8.20, 14.3, 15.6, 17.0, *d*, 24.8[e]	4.65

[a] Obeys the Curie–Weiss law for 78–300°K, $\Theta = -10°$. [b] Spectra of two D_2O analogs identical with those of the hydrates. [c] Asymmetric toward low frequency. [d] Several weak, spin-forbidden bands were observed above 20,000 cm^{-1} but have been omitted for brevity. [e] Charge transfer.

difference in π-donor capacity between the imidazole and chloride ligands or that the metal–anion distance is unusually great. For the hydrated compounds the average ligand field is stronger ($\Delta \sim 9700$ cm^{-1}) than for NiL_4Cl_2 (L = imidazole). This fact and the similarity between the two hydrates suggest that the water molecules occupy the axial positions in these complexes.

A bending mode of the O–M–O group is expected to contribute to the set of bands above 200 cm^{-1}. The corresponding vibrations for some hydrated trivalent metal ions have been observed[12,13] near 300 cm^{-1}. No band was observed near 400 cm^{-1}, where the M–O stretch occurs for the $M(H_2O)_6^{2+}$ ions,[14] but a band near 550 cm^{-1} for the nickel compounds is sensitive to deuteration. This band is in the range found for the H_2O wagging vibration of some hydrated ions,[14] but the shift on deuteration (Table VI) is much smaller than that previously observed for this mode and is close to the value (0.96) found[14] for the Ni–O stretch.

TABLE VI

SHIFT ON DEUTERATION OF THE 550-CM^{-1} BAND IN $[NiL_4(H_2O)_2]X_2$

X	H_2O	D_2O	Ratio
Cl	563	532	0.945
Br	540	520	0.963

Polymeric Octahedral Complexes.—Polymeric complexes of the stoichiometry ML_2X_2 are found for manganese(II) and of the type MLX_2 for manganese(II) and nickel(II). The compound MnL_2I_2 was unstable in air and gave a poor spectrum with broad bands. The other MnL_2X_2 compounds show absorption (Table IV) at about 250 cm^{-1} in the infrared spectrum, probably owing to the asymmetric Mn–L stretch of the *trans*-MnL_2X_4 unit. In the thiocyanate the band is broad and may contain also an Mn–NCS stretch. Absorption at 464 cm^{-1} in this compound is attributed to the N–C–S bending mode of the bridging thiocyanate group.

For the compounds MLX_2, it is likely that an M–L stretching vibration contributes to the highest energy band in each case. A number of infrared–Raman coincidences are observed as would be expected.

Square Compounds.—The changes both from six- to four-coordination and from high to low spin, with consequent shortening of the M–L bond, would be expected to raise the frequencies of the ν(M–L) vibrations for $[NiL_4]X_2$ (X = Br, I) compared with those in the compounds previously discussed.

Accordingly, we assign the bands at ~390 and ~330 cm^{-1} in their infrared spectra as the split components of the asymmetric Ni–L stretch of the cation (ν_6 (E_u) in D_{4h}). The infrared band at ~130 cm^{-1} may be the in-plane L–Ni–L bend (ν_7 (E_u) in D_{4h}) which from the results for $M(NH_3)_4{}^{2-}$ ions[15] would be expected to be below 200 cm^{-1}. Available evidence[16] suggests that the highest frequency Raman band of a square ML_4 species is ν_1 (A_{1g}) with ν_5 (B_{2g}) at slightly lower frequencies. On this basis the bands at 289 and 239 cm^{-1} (X = Br) and 288 and 236 cm^{-1} (X = I) may be ν_1 and ν_5, respectively. Against this, however, are the facts that these bands are at appreciably lower frequency than the infrared bands assigned as ν(Ni–L) and that the band in the 280–290-cm^{-1} region is relatively weak.

Tetrahedral Complexes.—The compound ZnL_2Cl_2 is known[17] to be tetrahedral and from their electronic spectra the 2:1 cobalt halide complexes also have this structure (Table V). The zinc bromide and iodide compounds have vibrational spectra (Table VII) which again indicate pseudo-tetrahedral configuration.

For the chlorides and iodides the two ν(M–L) modes may be assigned without much ambiguity, but for the bromides they lie close to the ν(M–Br) region and coupling must be appreciable.

Only for the zinc chloride complex could reliable Raman results be obtained above 200 cm^{-1}, and for this compound there was satisfactory agreement between the results from the two techniques. (The nonobservation of ν(Zn–L) and ν(Zn–X) in the Raman spectra of the zinc bromide and iodide complexes emphasizes the need for caution in interpreting the solid-state Raman data of, *e.g.*, the diamagnetic compounds $[NiL_4]X_2$ discussed above.) For ZnL_2Cl_2 the relative intensities of the Raman bands suggest that the symmetric Zn–Cl stretch lies at higher energy than the antisymmetric stretch, whereas with the zinc–imidazole bond the antisymmetric stretching mode lies higher. The intensity pattern in the infrared spectrum is very similar to that of CoL_2Cl_2.

Compounds $ML_2(NO_3)_2$.—The electronic spectrum of the complex $CoL_2(NO_3)_2$ suggests that it is six-coordinate with chelating nitrate groups, and the frequencies of the nitrate bands of this compound and its

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TABLE VII

VIBRATIONAL SPECTRA (CM^{-1}) AT 70–400 CM^{-1} FOR SOME TETRAHEDRAL IMIDAZOLE COMPLEXES

		ν(M–L)	ν(M–X)	Other bands
$\mathrm{CoL_2Cl_2}$	Ir	274 mw, 242 w	321 s, 308 s	196 mw, 165 s, 153 sh, 122 m, 105 sh
$\mathrm{CoL_2Br_2}$	Ir	(284 mw, 260 s, 255 sh)[a]		193 s,[b] 183 m, 165 w, 155 m
$\mathrm{CoL_2I_2}$	Ir	283 w, 252 m	237 ms	182 ms,[b] 168 mw, 148 m
$\mathrm{ZnL_2Cl_2}$	Ir	251 mw, 236 w	300 vs, 288 vs	199 ms, 160 m, br, 124 m, 102 w
	R	250 w, 239 m	296 vs, 286 w	216 w, 198 m, 177 w, 159 s, 105 s
$\mathrm{ZnL_2Br_2}$	Ir	(255 sh, 242 vs, 224 mw)[a]		190 s,[b] 158 m, 150 m, 111 w
	R			189 s,[b] 157 w
$\mathrm{ZnL_2I_2}$	Ir	251 m, 232 m	210 s	180 m,[b] 169 m, 148 mw
	R			178 w,[b] 166 m, 145 vs

[a] Bands in parentheses are considered to be due to strongly coupled ν(M–L) and ν(M–X) modes. [b] Possibly a component of ν(M–X).

TABLE VIII

VIBRATIONAL SPECTRA (CM^{-1}) AT 70–350 CM^{-1} FOR $\mathrm{ML_2(NO_3)_2}$ (M = Co, Cu, Zn)

$\mathrm{CoL_2(NO_3)_2}$	Ir	323 vs, 298 m, 278 s, 236 sh, 188 sh, 174 s, 145 m, br, 98 m, br
$\mathrm{CuL_2(NO_3)_2}$	Ir	330 s, 296 s, 246 w, 233 sh, 222 s, 203 ms, 146 m, 133 m, 103 m
$\mathrm{ZnL_2(NO_3)_2}$	Ir	288 s, 250 m, br, 188 w, 169 ms, 144 ms, 131 m, 100 w
	R	245 m, 190 sh, 172 s

zinc analog are very similar. This similarity does not, however, extend to the results in the low-frequency region (Table VIII).

The bands observed between 200 and 350 cm^{-1} almost certainly arise from ν(M–L) and ν(M–O) modes. It is likely that metal–oxygen stretching vibrations contribute appreciably to the highest energy bands, but there will be extensive coupling, and attempts at formal assignments to any particular, idealized mode seem unjustified.

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Notes

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Methylation of Deprotonated Ethylenediamine Complexes of Platinum(II) and Palladium(II)[1]

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It has recently been demonstrated[2] that the acidity of the en ligand in $\mathrm{[Pt(bipy)(en)]I_2}$ is markedly enhanced by the presence of the associated bipy ligand. Thus $\mathrm{Pt(bipy)(en)^{2+}}$ is deprotonated by liquid ammonia while $\mathrm{[Pt(en)_2]I_2}$ requires the more strongly basic amide ion.[3] Methylation of the deprotonation products of $\mathrm{Pt(bipy)(en)^{2+}}$ served to establish the sites of the successive deprotonations.[2] This work brought into question the possible effect of the bipy ligand upon the reactivity of the deprotonated species in the methylation reaction, particularly since earlier efforts[4] to methylate $\mathrm{Pt(en)(en\text{-}H)^{2+}}$ were unsuccessful. Accordingly it was of interest to reexamine the methylation of deprotonated species derived from $\mathrm{Pt(en)_2^{2+}}$ and the analogous palladium(II) complexes which are known[5] to differ from the corresponding platinum(II) complexes with regard to both stability and reactivity.

The results given below show that both $\mathrm{[Pt(en\text{-}H)(en)]I}$ and $\mathrm{[Pd(en\text{-}H)(en)]I}$ are methylated with methyl iodide under very mild conditions. It must therefore be concluded that an associated π-bonding ligand such as bipy is not a major determinant in the occurrence of the methylation process *per se*.

With reference to the identity of the isomer formed upon methylation of doubly deprotonated $\mathrm{[Pd(en)_2]I_2}$, $\mathrm{[Pd(udmen)(en)]I_2}$ is eliminated because of its instability when exposed to the atmosphere; $\mathrm{[Pd(men)_2]I_2}$ is also eliminated because of lack of correspondence of X-ray diffraction and infrared spectral data (Figure 1) for the two products. The same kinds of data, however, show that the methylation product is $\mathrm{[Pd(sdmen)(en)]I_2}$; this conclusion also removes from consideration the removal of one proton from each en ligand in either the *cis* or *trans* positions.

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[1] Abbreviations: en, ethylenediamine; en-*x*H, an en ligand from which *x* protons have been removed; men, N-methylethylenediamine; dmen, a dimethylethylenediamine complex with the position of the methyl groups unspecified; sdmen, N,N′-dimethylethylenediamine; udmen, N,N-dimethylethylenediamine; bipy, 2,2′-bipyridyl.

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