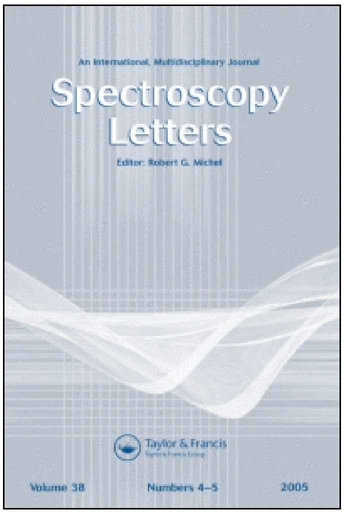

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Fourier Transform Infrared and Raman Spectra of Metal Halide Complexes of 3,5-Lutedine in Relation to Their Structures

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FOURIER TRANSFORM INFRARED AND RAMAN SPECTRA OF METAL HALIDE COMPLEXES OF 3,5-LUTIDINE IN RELATION TO THEIR STRUCTURES

Keywords: Infrared and Raman spectra, 3,5-lutidine metal halide complexes.

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ABSTRACT

Fourier transform infrared (4000-200 cm^{-1}) and Raman (3500-50 cm^{-1}) spectra are reported for metal(II) halide 3,5-lutidine (3,5-dimethylpyridine) complexes of the following stoichiometries: $M(3,5L)_4X_2$ M=Co or Ni, X=Cl or Br; M=Mn or Cu, X=Br; M=Cd, X=I; $M(3,5L)_3X_2$ M=Fe, X=Cl; M=Cu, X=Br; $Hg(3,5L)X_2$ X=Cl or Br.

Vibrational assignments are given for all the observed bands. Some structure-spectra correlations are found. For a given series of isomorphous complexes the sum of the difference between the liquid and ligand values of the vibrational modes of 3,5-lutidine is found to increase in the order of the second ionization potentials of the metals. The frequency shifts are also found to depend on the halogen.

INTRODUCTION

To the best of our knowledge no infrared and Raman measurements have been reported for the metal(II) halide 3,5-lutidine (3,5-dimethylpyridine) complexes.

In this work the infrared and Raman spectra of the transition metal complexes of 3,5-lutidine have been systematically investigated in an effort to establish a relationship between the ligand vibrational wavenumbers and the metal-ligand strength. The effective magnetic moments of the complexes have also been measured.

RESULTS AND DISCUSSION

Although most metal halide pyridine complexes have been characterised crystallographically, there is a distinct lack of structural data for 3,5-lutidine halide complexes. However since isostructural complexes are known to exhibit similar band patterns in their vibrational spectra[1-3], in the absence of structural data on a given complex, it has been classified depending on its spectroscopic features.

The $Hg(3,5L)X_2$ (X=Cl or Br), $Fe(3,5L)_3Cl_2$ and $Cu(3,5L)_3Br_2$ complexes have been prepared for the first time. They are assumed to have dimeric structures based on an octahedral geometry around each metal atom, similar to the corresponding pyridine and aniline halide complexes[1,4]

The $Co(3,5L)_4X_2$ (X=Cl or Br) and $Ni(3,5L)_4Cl_2$ complexes are known to have a monomeric octahedral configuration[5-7]. The $M(3,5L)_4X_2$ (M=Ni,Mn or Cu; X=Br; and M=Cd, X=I) complexes, except for M=Ni, have been prepared for the first time. Although there is no structural data on these complexes, since the band patterns of their IR and Raman spectra are found to be similar to those known to have monomeric octahedral structures, they are also assumed to have a monomeric trans octahedral structure similar to that of 4-methylpyridine halide complexes[2].

A detailed IR and Raman spectroscopic study on the methylpyridines has been reported by Green et al.[8], with a more recent theoretical calculation by Draeger[9]. Since Draeger's assignment for 3,5-lutidine is consistent with that of Green et al., the latter's assignment was used. The IR and Raman spectra of the mono-, tri- and tetra- 3,5-lutidine complexes are given in Tables 1-2. The IR and Raman spectra of liquid 3,5-lutidine taken from Green et al's paper[8] are included in Table 1 for comparison. As can be seen from the tables, several vibrational modes of 3,5-lutidine have upward shifts in frequency when compared with the liquid 3,5-lutidine values. These shifts in frequency (compared to Green et al's values for liquid 3,5-lutidine) were summed for all the available ring and CH modes of 3,5-lutidine observed in the IR spectra of the complexes namely, all the modes except the CH_3 group vibrational modes and ν_1, ν_{12} and ν_{26}. Summing the shifts in this way will tend to average out random errors arising in the measurement of each band and make the metal dependence of the shifts clearer. The total shifts are given at the bottom of Tables 1-2. It should thus be possible to compare the shift values of isomorphous complexes as well as observing for a given metal the effect of changing the stoichiometry of the complex and of changing the counter ligand from Cl to Br. These shift values for isomorphous complexes show a progressive increase on going across the period from Mn to Cu and

TABLE 1

Infrared and Raman spectra of dimeric 3,5-lutidine complexes (values in cm^{-1})

Assignment[a]	Liquid 3,5-lutidine[a]		$Hg(3,5L)Cl_2$		$Hg(3,5L)Br_2$		$Fe(3,5L)_3Cl_2$		$Cu(3,5L)_3Br_2$	
	IR	R	IR	R	IR	R	IR	R	IR	R
$\nu_1(a_1)$		3047	3062				3073	3076	3078	3079
$\nu_2(a_1),\nu_{19}(b_2)$	3029	3023	3038		3029	3031	3015	3017	3031	3028
$\nu_3(a_1)$	1602	1599	{1601 1594	1603	{1614 1595	1599	1598	1599	1607	1605
$\delta_a(CH_3),\nu_4(a_1)$	1463	1452	1461		1461		{1458 1443		1462	
$\nu_{21}(b_2)$	1426	1432	{1446 1439		1437		1426		1451	
$\nu_{22}(b_2)$	1320	1322	1331		1327		1322	1321	{1334 1326	
$\nu_5(a_1)$	1273	1270	1289	1280	1276	1279	1274	1276	1281	1282
$\nu_{23}(b_2)$	1232	1234	1252		1253		1246		1249	
$\nu_{24}(b_2)$	1164	1166	1168		1168	1170	1179	1182	1184	
$\nu_6(a_1)$	1138	1139	1140		1140		1153	1156	1157	
$\nu_7(a_1)$	1032	1032	1033	1036	1033	1034	1035	1038	1035	1037
$\nu_{25}(b_2)$	1011		1018		1018		1019		1019	
$\nu_{11}(a_2)$	944		945		955		942	948	949	
$\nu_{14}(b_1)$	929	935	938		938		937	936	937	
$\nu_{15}(b_1)$	857	864	864		863	865	866	860	865	
$\nu_8(a_1)$	715	719	{761 747	754	{751 746	752	744	747	{773 765	771
$\nu_{16}(b_1)$	710		{703 699		{703 698		703		{701 694	
$\nu_9(a_1)$	539	537	537	539	537	539	536	547	540	543
$\nu_{26}(b_2)$	532									
$\nu_{12}(a_2)$	498	498								
$\nu_{27}(b_2)$	395	397	416		412		415	419	423	
$\nu_a(CH_3)$	{2985 2971	{2987 2953	{2965 2954		{2965 2953		2946	2950	{2969 2949	
$\nu_s(CH_3)$	2930	2920	2919		2918	2922	2913	2917	2914	2916
$2\delta_a(CH_3)$	2896		2864		2863	2865	2864	2865	2867	
$2\delta_s(CH_3)$	2738		2737		2734		2745		2735	
$\delta_a(CH_3),\nu_4(a_1)$	1463	1452	1458		1461		{1458 1443		1462	
$\delta_s(CH_3)$	1379	1380	{1384 1374		{1383 1376	1382	1384	1390	1377	
CH_3 rock	1043		1045		1043		1049		1045	
Total shift			146		122		81		207	
μ_{eff}(B.M.)			n.m		n.m		4.29		1.87	

[a] Wavenumbers and the assignment are taken from ref.11.
n.m = not measured.

TABLE 2

Infrared and Raman spectra of monomeric octahedral tetra-(3,5-lutidine) complexes

Assignment	$Co(3,5L)_4Cl_2$		$Co(3,5L)_4Br_2$		$Ni(3,5L)_4Cl_2$	
	IR	R	IR	R	IR	R
$\nu_1(a_1)$	3076	3078	3076	3077	3080	3078
$\nu_2(a_1),\nu_{19}(b_2)$	3015	3019	3014	3016	3015	3020
$\nu_3(a_1)$	1599	1600	1599	1598	1600	1601
$\delta_a(CH_3),\nu_4(a_1)$	1457 1446	1460	1459		1467 1456	
$\nu_{21}(b_2)$	1427		1430		1448	
$\nu_{22}(b_2)$	1321		1323		1321	
$\nu_5(a_1)$	1276	1277	1276	1276	1279	1280
$\nu_{23}(b_2)$	1246	1251	1247		1246	
$\nu_{24}(b_2)$	1181	1184	1181		1186	1188
$\nu_6(a_1)$	1154	1159	1154	1158	1156	1163
$\nu_7(a_1)$	1036	1038	1036	1037	1036	1039
$\nu_{25}(b_2)$	1020	1026	1019		1020	
$\nu_{11}(a_2)$	945	958	939		940	
$\nu_{14}(b_1)$	937	930	925		926	930
$\nu_{15}(b_1)$	866		866		867	
$\nu_8(a_1)$	748	752	749	751	751	757
$\nu_{16}(b_1)$	704		704		704	
$\nu_9(a_1)$	537	547	537	547 530	538	547
$\nu_{12}(a_2)$	496	504		502		
$\nu_{27}(b_2)$	418	419	418		421	
$\nu_a(CH_3)$	2972 2969	2977 2952	2945		2971 2949	
$\nu_s(CH_3)$	2912	2916	2912	2914	2914	
$2\delta_a(CH_3)$	2864		2864	2860	2865	
$2\delta_s(CH_3)$	2746		2743		2746	
$\delta_a(CH_3),\nu_4(a_1)$	1457 1446	1460	1459		1467 1446	
$\delta_s(CH_3)$	1396 1384	1390	1395 1383	1387	1400 1384	1389
CH_3 rock	1049		1049		1048	
Total shift	103		97		137	
μ_{eff}(B.M.)	4.50		4.72		n.m	

n.m = not measured. d.= diamagnetic.

(continued)

TABLE 2 continued

Infrared and Raman spectra of monomeric octahedral tetra-(3,5-lutidine) complexes

Assignment	$Ni(3,5L)_4Br_2$		$Mn(3,5L)_4Br_2$		$Cu(3,5L)_4Br_2$		$Cd(3,5L)_4I_2$	
	IR	R	IR	R	IR	R	IR	R
$\nu_1(a_1)$		3084	3067		3077	3084	3052	
$\nu_2(a_1),\nu_{19}(b_2)$	3013	3017	3010	3016	3030	3015	3016	3015
$\nu_3(a_1)$	1599	1601	1598	1600	1605 1597	1599	1596	1598
$\delta_a(CH_3),\nu_4(a_1)$	1463		1458		1456		1469	
$\nu_{21}(b_2)$	1441		1438 1427		1448	1424	1436	
$\nu_{22}(b_2)$	1323		1325		1326		1326	
$\nu_5(a_1)$	1277	1281	1287 1274	1277	1280	1284	1283 1270	1286 1273
$\nu_{23}(b_2)$	1246		1248		1249	1251	1250	
$\nu_{24}(b_2)$	1186	1188	1175	1180	1186	1179	1172	1176
$\nu_6(a_1)$	1156		1151	1156	1157	1163	1148	1146
$\nu_7(a_1)$	1037	1039	1034	1037	1034	1037	1032	1034
$\nu_{25}(b_2)$	1020		1018		1021		1013	
$\nu_{11}(a_2)$	940	939	945		951		943	
$\nu_{14}(b_1)$	925	927	927		942	942	926	
$\nu_{15}(b_1)$	867		865		868	867	863	
$\nu_8(a_1)$	752	757	746	748	765	770	743	745
$\nu_{16}(b_1)$	705	710	703		701 694	708	701	
$\nu_9\ (a_1)$	537	547	535	547 540	537	544	533	545 536
$\nu_{12}(a_2)$		507				479		
$\nu_{27}(b_2)$	420		411	418	422	415	406	
$\nu_a(CH_3)$	2973 2946		2944		2968 2947	2951	2972	
$\nu_s(CH_3)$	2913	2916	2912	2914	2911	2915	2912	2915
$2\delta_a(CH_3)$	2864	2865	2864		2865	2868	2861	
$2\delta_s(CH_3)$	2743		2744		2745		2739	
$\delta_a(CH_3),\nu_4(a_1)$	1463		1458		1456		1469	
$\delta_s(CH_3)$	1399 1383	1389	1383	1390	1397 1383	1391	1381	1386
CH_3 rock	1050		1049		1048		1050	
Total shift	129		84		191		71	
μ_{eff}(B.M.)	2.95		5.51		1.81		d.	

n.m = not measured. d.= diamagnetic.

this correlates with the increase in the second ionisation potential of the metals. Similar shifts were observed in the vibrational spectra of pyridine and pyridine derivative halide complexes[1-3] and explained by a mechanical coupling of pyridine (or pyridine derivative) vibrations with M-N (pyridine or pyridine derivative) vibrational modes[1-3,10]. Therefore we infer that the M-N(lutidine) bond strength and thus the M-N(lutidine) stretching mode frequency increase in the same order. It is also noted that for the isomorphous complexes the shift values depend on the halogen, for a given metal it decreases in the order Cl > Br.

The magnetic susceptibilities of the powdered samples were measured on a Gouy balance at room temperature. The values are presented at the bottom of Tables 1-2. These values are found to be similar to those of analogous compounds[6-7].

EXPERIMENTAL

The complexes were prepared by addition of the appropriate quantity of 3,5-lutidine to a saturated solution of the metal chloride in ethanol. The precipitated complexes were filtered, washed with ether and finally dried.

The halide contents were determined using potentiometric titration with silver nitrate. Carbon, hydrogen and nitrogen were determined by standard microanalytical-procedures in the laboratories of J.E.D. Davies. Magnetic susceptibility measuremets were made by the Gouy method.

The IR spectra of complexes were recorded on Nicolet MX-IE, and Perkin-Elmer 1430 spectrometers which were calibrated using CO_2 and polystyrene bands.

The Raman spectra were excited using either the 488.0 nm or 514.5 nm lines of a CRL Ar^+ ion gas laser and recorded on a Cary 81 Spectrometer. The spectrometer was calibrated using neon emission lines.

TABLE 3

Analytical data for compounds prepared

Compound	C(%)	H(%)	N(%)	Halogen(%)
	Found (Cal)	Found(Cal)	Found(Cal)	Found(Cal)
$Hg(3,5L)\ Cl_2$	23.28(22.20)	2.30(2.40)	3.87(3.70)	n.m
$Hg(3,5L)\ Br_2$	20.26(17.97)	1.78(1.94)	3.38(3.00)	n.m
$Cu(3,5L)_3Br_2$	44.35(46.29)	4.23(5.01)	7.36(7.71)	30.19(29.33)
$Fe(3,5L)_3Cl_2$	57.92(56.30)	6.32(6.03)	9.50(9.37)	n.m
$Co(3,5L)_4Cl_2$	n.m	n.m	n.m	12.54(12.70)
$Co(3,5L)_4Br_2$	51.57(51.97)	5.74(5.62)	8.41(8.66)	23.87(24.69)
$Ni(3,5L)_4Cl_2$	59.70(60.24)	6.87(6.51)	9.62(10.04)	12.17(12.70)
$Ni(3,5L)_4Br_2$	49.68(51.96)	5.68(5.62)	8.95(8.66)	24.09(24.70)
$Mn(3,5L)_4Br_2$	51.64(52.27)	5.62(5.65)	8.37(8.71)	24.43(24.84)
$Cu(3,5L)_4Br_2$	51.63(51.58)	4.98(5.58)	8.34(8.60)	24.74(24.51)
$Cd(3,5L)_4I_2$	41.91(42.31)	4.53(4.57)	6.88(7.05)	31.43(31.93)

n.m= not measured

The results of C, H, N and halogen analyses for the samples are given in Table 3.

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