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Infrared Spectra of Hydroxy-Bridged Copper(II) Compounds[1]

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Received April 1, 1965

The infrared spectra of hydroxy-bridged copper(II) compounds from 4000 to 70 cm.$^{-1}$ have been obtained. Frequency assignments are suggested for the hydroxyl and the copper–oxygen vibrations in the bridge and the copper–nitrogen vibration to the organic ligand. The effect of the environment around the anion in these complexes is also discussed.

Introduction

Walker[2] prepared and investigated compounds of the type $[(\text{chelate})\text{Cu}<^{\text{OH}}_{\text{OH}}>\text{Cu}(\text{chelate})]\text{Yn}\cdot Z\text{H}_2\text{O}$ where chelate = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy) and Yn and Z are as shown in Table I. The proposed hydroxy-bridged structure rather than the monomeric structure $(\text{chelate})\text{Cu}<^{\text{OH}}_{\text{Y}}$ was supported by chemical and physical evidence.[2] A detailed report of that investigation is to be published elsewhere.[3]

The infrared spectra of hydroxy-bridged complexes of transition metals have not been extensively investigated, although studies on related metal complexes with 2,2′-bipyridyl[4-7] and 1,10-phenanthroline[7-11] have been reported. Related studies of copper complexes with 2-methyl and 2-aminopyridine have been reported by McWhinnie.[12] Extension of these studies to the infrared region beyond 600 cm.$^{-1}$ has occurred only very recently. Inskeep and Benson[8] reported the spectrum of $[(\text{phen})_2\text{CrOH}]_2(\text{NO}_3)_4$ to 250 cm.$^{-1}$ but made no interpretations for the bands found in this region. Goldstein and co-workers[13] investigated Cu(II) complexes of heterocyclic bases down to 20 cm.$^{-1}$. Inskeep[11] also reported the spectra of the tris complexes of 1,10-phenanthroline and 2,2′-bipyridyl with the transition metals to 250 cm.$^{-1}$. McWhinnie[14] has published infrared spectra of related compounds down to 222 cm.$^{-1}$. Several important aspects of these compounds remain unsolved. These include (1) the position of the OH vibrations, (2) the metal–oxygen vibrations, and (3) the M–N vibrations to the organic ligand. The purpose of this study was to measure the infrared spectra of these complexes to 70 cm.$^{-1}$ and to attempt to find the Cu–O and the Cu–N vibrations. In addition a search for the OH vibrations was made. The effect of environment of the anion in these complexes, as determined from the infrared spectra, was also examined.

TABLE I

ANALYTICAL RESULTS OF THE COMPOUNDS $[\text{XCu}<^{\text{OH}}_{\text{OH}}>\text{CuX}]\text{Yn}\cdot Z\text{H}_2\text{O}$

				C, %		H, %		N, %		Cu, %		X, %	
Compd.	X	Yn	Z	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
A	bipy	SO_4	5	36.3	36.4	4.5	4.3	8.6	8.5	19.5	19.3		
B	bipy	I_2	3	30.5	30.7	3.4	3.1	6.8	7.2	16.6	16.3	32.9	32.5
C	bipy	Br_2	4	34.2	34.1	3.7	3.7	7.9	8.0	18.1	18.0	23.9	23.7
D	bipy	$(ClO_4)_2$	1	35.3	34.8	3.1	2.9	8.2	8.1	18.8	18.4		
E	bipy	$PtCl_4$	3	27.2	27.8	2.6	2.8	6.4	6.5				
F	bipy	Cl_2	3	39.6	40.2	4.2	4.0	9.0	9.4	20.8	21.2		
G	bipy	$(SCN)_2$	1	43.4	43.5	3.3	3.3	14.2	13.8	21.2	20.9		
H	bipy	$(PF_6)_2$	2	31.6	30.1	2.7	2.8	7.3	7.0	15.8	15.9		
I	phen	SO_4	5	40.5	40.7	4.1	4.0	8.3	7.9	18.1	18.0		
J	phen	I_2	2	36.7	35.5	2.5	2.7	6.0	6.9	15.9	15.7	31.5	31.3
K	phen	Br_2	4	38.1	38.3	3.4	3.5	7.2	7.4	17.6	16.9		
L	phen	$(ClO_4)_2$	0	38.5	38.1	3.1	2.9	7.4	7.4	17.2	17.6		
M	phen	Cl_2	3	44.7	44.6	4.0	3.7	...	...	19.4	19.7		
N	phen	$(SCN)_2$	2	46.8	46.3	3.1	3.3	12.7	12.5	18.6	18.9		

Experimental

The preparation of these complexes has been described,[2] and the elemental analyses are tabulated in Table I. The analyses for C, H, N, and the halogens were made by standard microanalytical techniques.[15] The copper analyses were made

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[1] Based on work performed under the auspices of the U S. Atomic Energy Commission.

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[13] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

[14] W R. McWhinnie, *J. Inorg. Nucl. Chem.*, **27**, 1063 (1965).

[15] Microanalyses were made by Drs. Challen (University of New South Wales, Australia) and Zimmerman (C.S.I.R.O., Australia).

TABLE II

ABSORPTION FREQUENCIES OF COPPER COMPOUNDS FROM 4000 TO 70 CM.$^{-1}$

bipy	A	B	C	D	E	F	G	H	phen	I	J	K	L	M	N
3080(VW)	3440(Sh)	3430(Sh)	3440(Sh)	3440(Sh)	3550(Sh)	3430(Sh)	3515(M)(B)	3601(W)	3044(W)	3400(Sh)	3480(Sh)	3350(VS)(B)	3400(S)	3400(Sh)	3525(Sh)
3050(VW)	3348(VS)(B)	3380(VS)(B)	3370(S)(B)	3353(VS)(B)	3425(S)(B)	3348(S)(B)	3105(VW)	3420(M)(B)	3030(W)	3325(S)(B)	3375(S)(B)	3050(VW)	3340(S)	3390(S)(B)	3490(M)
1580(S)	3103(VW)	3100(W)	3106(VW)	3106(W)	3100(VW)	3108(VW)	3073(VW)	3101(VW)	1609(W)	3052(W)	3035(VW)	1621(VW)	3054(W)	3049(W)	3059(W)
1553(M)	3048(VW)	3050(W)	3020(VW)	3062(VW)	3072(VW)	3070(VW)	2115(W)	3030(VW)	1584(M)	1625(W)	1620(W)	1583(VW)	1651(W)	1623(W)	2117(M)
1450(S)	3017(W)	3020(W)	1650(W)(B)	3021(W)	1635(Sh)	3023(VW)	2080(S)	2922(VW)	1556(W)	1584(W)	1575(W)	1516(M)	1645(W)	1603(VW)	2089(S)
1415(S)	1642(Sh)	1606(Sh)	1620(W)	1635(Sh)	1607(Sh)	1620(VW)	1605(Sh)	1612(Sh)	1499(S)	1516(M)	1516(M)	1430(S)	1622(W)	1584(M)	1621(W)
1270(VW)	1617(M)	1599(S)	1599(M)	1615(M)	1598(S)	1600(M)	1598(M)	1605(M)	1445(W)	1485(VW)	1429(M)	1343(VW)	1604(W)	1516(Sh)	1580(W)
1250(M)	1607(Sh)	1564(VW)	1562(VW)	1606(Sh)	1572(VW)	1560(W)	1573(VW)	1567(W)	1415(S)	1431(M)	1342(VW)	1218(VW)	1584(M)	1489(W)	1516(M)
1210(VW)	1596(VS)	1494(M)	1493(W)	1599(VS)	1564(VW)	1493(VW)	1565(VW)	1498(W)	1339(W)	1345(VW)	1195(VW)	1196(VW)	1516(S)	1431(S)	1490(W)
1138(VW)	1566(M)	1471(M)	1472(W)	1566(W)	1493(W)	1471(W)	1491(VW)	1475(M)	1206(VW)	1221(VW)	1145(W)	1145(W)	1490(W)	1427(Sh)	1426(S)
1120(VW)	1494(S)	1445(S)	1445(M)	1494(M)	1472(W)	1440(M)	1469(W)	1446(S)	1131(W)	1162(M)	1134(W)	1134(W)	1431(VS)	1350(W)	1340(W)
1080(M)	1473(S)	1315(M)	1323(W)	1473(M)	1445(S)	1317(VW)	1445(M)	1317(M)	1087(M)	1150(M)	1103(W)	1103(W)	1343(VW)	1221(VW)	1219(VW)
1060(VW)	1443(VS)	1250(W)	1317(W)	1445(VW)	1310(M)	1250(VW)	1311(W)	1250(W)	1061(VW)	1134(M)	902(VW)	919(W)	1222(M)	1194(VW)	1147(VW)
1040(W)	1325(M)	1170(VW)	1251(VW)	1325(M)	1252(VW)	1173(VW)	1248(W)	1172(VW)	1021(VW)	1075(VS)	868(W)	869(Sh)	1145(M)	1148(W)	1130(VW)
990(W)	1318(M)	1157(W)	1170(VW)	1318(M)	1166(W)	1160(W)	1169(VW)	1160(W)	989(VW)	1043(VS)	854(M)	861(Sh)	1100(VS)	1138(Sh)	1101(VW)
890(VW)	1252(M)	1101(W)	1159(W)	1252(W)	1154(W)	1102(VW)	1159(VW)	1103(W)	876(Sh)	1030(VS)	777(W)	853(M)	1058(S)	1103(W)	860(Sh)
751(S)	1132(S)	1071(VW)	1101(VW)	1170(W)	1102(W)	1026(W)	1094(VW)	1066(VW)	856(S)	990(VW)	735(W)	777(W)	1032(M)	1034(VW)	846(S)
738(Sh)	1120(S)	1026(M)	1025(W)	1158(W)	1030(W)	1012(W)	1026(VW)	1045(VW)	849(S)	909(VW)	721(S)	735(W)	950(VW)	1000(W)	770(W)
657(M)	1090(VS)	1014(W)	1014(W)	1122(M)	1016(W)	949(VW)	868(W)	1032(VW)	838(S)	870(M)	650(W)	722(S)	920(VW)	910(VW)	734(W)
622(M)	1065(VS)	960(VW)	905(VW)	1100(Sh)	900(VW)	900(VW)	767(Sh)	910(M)	764(M)	848(S)	498(VS)(B)	625(W)(B)	868(S)	870(M)	718(M)
404(S)	1030(VS)	860(VW)	887(M)	1080(VS)	846(VW)	768(M)	762(M)	890(M)	743(M)	772(W)	440(Sh)	510(Sh)	849(VS)	849(S)	650(W)
164(S)	1013(M)	766(S)	768(M)	1068(VS)	770(M)	739(W)	730(M)	830(VS)	730(M)	730(VW)	430(M)	492(S)	768(W)	772(M)	500(VW)
98(M)	970(W)	739(VW)	739(W)	1047(W)	730(M)	727(M)	660(M)	770(W)	718(M)	719(S)	301(M)	432(W)	734(W)	734(M)	482(M)
	955(W)	727(S)	727(M)	1032(W)	665(W)	660(M)	654(M)	765(M)	700(M)	651(VW)	251(M)	300(M)	717(VS)	650(W)	465(M)
	919(VW)	658(M)	660(M)	1025(M)	652(W)	650(Sh)	640(W)	759(M)	620(W)	620(VS)	229(M)	285(VW)	640(VW)	575(M)(B)	432(M)
	905(VW)	635(M)	655(Sh)	1014(M)	642(W)	619(S)(B)	488(M)	737(M)	404(W)	575(W)	218(Sh)	271(VW)	622(VS)	547(W)	408(W)
	890(W)	478(S)	639(W)	983(W)	494(S)(B)	489(S)	468(M)	727(M)	257(W)	545(VW)	188(W)	257(M)	562(VW)	507(W)	319(M)
	803(VW)	468(S)	590(M)(B)	900(M)	444(W)	470(M)	430(Sh)	669(W)	240(M)	508(VW)	101(VW)	236(M)	508(M)	482(VS)	297(Sh)
	766(VS)	430(M)	540(VW)	880(VW)	423(M)	435(W)	417(M)	652(W)	146(M)	480(S)	85(VW)	216(W)	492(Sh)	433(W)	291(M)
	740(M)	412(S)	490(S)	800(VW)	324(S)	415(S)	265(W)	648(VW)	116(S)	430(W)		107(VW)	480(S)	300(W)	240(W)
	726(VS)	268(M)	470(S)	766(VS)	271(W)	268(M)	232(M)	560(VS)	89(W)	302(W)		87(VW)	430(W)	287(VW)	224(W)
	659(M)	<170cm^{-1}	435(W)	739(W)	152(VVW)	258(Sh)	143(VW)	490(S)		246(M)			303(W)	274(VW)	206(M)
	652(Sh)	Spectrum	417(S)	727(VS)		137(VW)		430(M)		200(M)			240(W)	258(VW)	191(VW)
	637(M)	Too diffuse	267(M)	662(M)		117(VW)		420(M)		151(M)			Spectrum	252(VW)	174(VW)
	618(VS)		258(M)	655(Sh)		92(VW)		278(M)		117(M)			not run	240(M)	152(W)(B)
	585(M)		246(M)	640(VS)				212(Sh)		108(M)			below 170	196(W)	117(W)
	490(S)		<170cm^{-1}	620(VS)				206(M)		89(M)			cm^{-1}	162(VW)	103(W)
	480(S)		Spectrum	590(M)				201(Sh)						128(W)	93(W)
	470(S)		Too diffuse	540(VW)				<170cm^{-1}						108(VW)(B)	
	430(M)			490(S)				Spectrum							
	414(S)			480(S)				Too diffuse							
	365(W)			433(M)											
	269(S)			418(S)											
	242(M)			387(W)											
	192(M)			370(W)											
	182(Sh)			277(W)											
	143(W)			224(W)											
	136(W)			152(VW)											
	114(W)			117(VW)											
				92(VW)											

[a] The absorption bands reported in this table are from spectra obtained with KBr disks and checked with Nujol mulls. Anion absorptions are based on Nujol mull spectra only. VS, very strong; S, strong; M, medium; W, weak; VW, very weak; Sh, shoulder; B, broad. Symbols in top column across corresponds to those used in Table I.

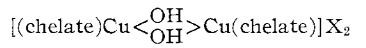
after fuming the complex with a H_2SO_4–$HClO_4$ mixture and then volumetrically titrating for Cu with KI–$Na_2S_2O_3$.

The spectra in the 4000–650 cm.$^{-1}$ infrared region were obtained with a Perkin-Elmer Model 421 spectrophotometer. The spectra in the region 650–350 cm.$^{-1}$ were obtained with a Beckman Model IR-7 spectrophotometer equipped with a CsI prism. The spectra in these regions were measured with KBr disks and checked by Nujol mulls. For the Nujol mulls BaF_2 windows were used in the NaCl region and polyethylene windows from 650 to 350 cm.$^{-1}$. The spectra in the region beyond 350 cm.$^{-1}$ were obtained with a Perkin-Elmer Model 301 spectrophotometer, where Nujol mulls were used with polyethylene windows.

The deuteration of several of the compounds was accomplished by recrystallization of the solid from D_2O. Ordinary contacting of the solid with excess D_2O failed to deuterate the bridging hydroxyl hydrogen, although the water of hydration was exchanged easily.

Results and Discussion

The infrared absorption frequencies from 4000 to 70 cm.$^{-1}$ of eight 2,2′-bipyridyl and six 1,10-phenanthroline complexes of copper are tabulated in Table II. The spectra of these complexes are quite complex, and, therefore, only suggested assignments are made. Molecular conductivities of these complexes in water at 25°[2] were found to be 220 mhos. This evidence, together with other physical evidence, such as magnetic moment studies and chemical studies, has led to the conclusion that these complexes are hydroxy-bridged, of the type



$$[(\text{chelate})\text{Cu}{<}^{\text{OH}}_{\text{OH}}{>}\text{Cu}(\text{chelate})]X_2$$

From this infrared study, the position of the hydroxy vibration in these compounds is tentatively assigned. In addition it can be established that the organic ligands are chelated to the metal and that bands in the far-infrared may be attributed to vibrations involving the M–N to the ligand and M–O to the hydroxyl group.

Table III

Suggested Assignments for the OH, Cu–O, and Cu–N Stretches in Copper Compounds (cm.$^{-1}$)

Compd.	OH str.	Asym. Cu–O str.[a]	Asym. Cu–N str.[a]
bipy	. . .	. . .	. . .
A	3440	490	269
B	3430	478	268
C	3440	490	267
D	3440	490	277
E	3550	494	271
F	3430	489	268
G	3515	488	265
H	3601	490	278
phen	. . .	. . .	. . .
I	3400	480	302
J	3480	498	301
K	3350	492	300
L	3400, 3340	480	303
M	3400	482	300
N	3525	482	291
$CuSO_4 \cdot 3Cu(OH)_2$[19]	3586, 3564 3390, 3270		
$Cu(NO_3)_2 \cdot 3Cu(OH)_2$[19]	3543, 3522 3428		

[a] Strongest band in this region. The symbols in column 1 corresponds to those used in Table I.

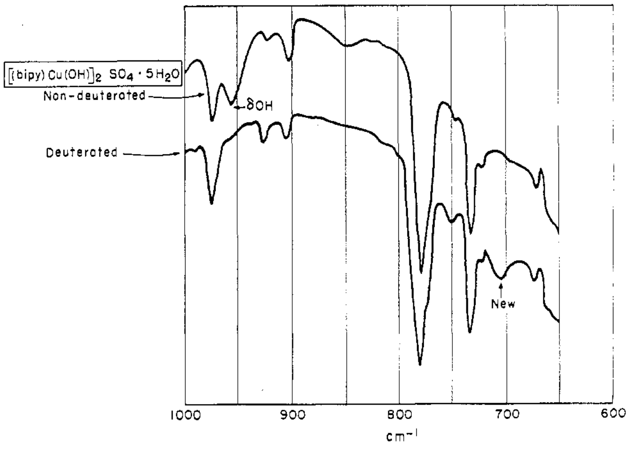


Figure 1.—Comparison of spectra of nondeuterated and deuterated $[(bipy)Cu(OH)]_2SO_4 \cdot 5H_2O$; Nujol mull spectra.

2,2′-Bipyridyl Complexes

OH Vibration.—Most of these compounds are hydrated, and this necessarily complicates interpretations made in the 3500 cm.$^{-1}$ region. In addition, the water band in this region is extremely broad and strong. However, in a number of instances a shoulder appears on the high-frequency side of this water band, and this can be assigned to the OH stretch in the bridging OH groups. The position of the shoulder is tabulated in Table III for the various complexes. It is observed that in $[(phen)Cu(OH)ClO_4]_2$, which is the only anhydrous complex, the bridge OH stretching vibration is a doublet at 3400 and 3340 cm.$^{-1}$. Support for this assignment comes from a very recent study by McWhinnie[12] of hydroxy-bridged copper complexes with 2-aminopyridine. Nakamoto[16] assigned a band at about 3300–3400 cm.$^{-1}$ in the $[(oxalate)Co(OH)]_2$ complex to the bridging OH stretching vibration. Scargill[17] reported OH stretching bands in the 3200–3500 cm.$^{-1}$ region in hydroxo complexes of ruthenium. In several hydroxides the vibration has been recorded at 3500–3700 cm.$^{-1}$.[18] Tarte[19] reports the OH vibration in basic copper salts also in this region.

The comparison of the deuterated and nondeuterated spectra of $[(bipy)Cu(OH)]_2SO_4 \cdot 5H_2O$ is shown in Figure 1. The band at 955 cm.$^{-1}$ in the nondeuterated form shifts to 710 cm.$^{-1}$ upon deuteration. The ratio of these bands is 1.34, which is what one expects for a deuterium shift. Support for the assignment of the bending OH vibration in this compound at 955 cm.$^{-1}$ comes from Nakamoto,[16] who reported the δOH absorption in $[(oxalate)Co(OH)]_2$ at about 1090 cm.$^{-1}$. In addition the bending OH vibrations in basic copper compounds[19] are reported in the region 1000–677 cm.$^{-1}$.

The 1000–1600 Cm.$^{-1}$ Region.—New bands are observed at about 1600, 1490, and 1470 cm.$^{-1}$ upon chela-

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[16] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, and personal communication.

[17] D. Scargill, *J. Chem. Soc.*, 4440 (1961).

[18] M. Cabannes-Ott, *Compt. rend.*, **242**, 355 (1956).

[19] P. Tarte, *Spectrochim. Acta*, **13**, 107 (1958).

tion of 2,2′-bipyridyl to copper. These are absorptions involving the ring C–C and C–N vibrations of the bipyridyl[20] and are observed at lower frequencies in the uncomplexed ligand. The water bending vibration occurs at about 1630 cm.$^{-1}$ as a shoulder to the strong band at about 1600 cm.$^{-1}$. Additional bands are found in the 1310–1325 cm.$^{-1}$ region, at 1160 cm.$^{-1}$, and in the 1013–1030 cm.$^{-1}$ region. The absorption in the 1000 cm.$^{-1}$ region has been assigned[5,20] to the pyridine breathing mode in the uncomplexed bipyridyl. Upon chelation the band shifts to higher frequency and intensifies. Sinha[5] has made similar observations on related complexes.

The 700–800 Cm.$^{-1}$ Region.—Upon chelation splitting of the out-of-plane CH bending vibrations at about 750 cm.$^{-1}$ occurs. Similar splitting has been observed in related complexes.[5,7,11]

Infrared Spectra, 650–70 Cm.$^{-1}$.—One of the features of the spectra in this region is strong absorption at 470–500 cm.$^{-1}$, which is absent in the bipyridyl spectrum. In some cases several strong bands are observed in this region. Considering a D_{2h} symmetry for these molecules having four Cu–O bonds, two infrared modes for a Cu–O stretch should be active. One of these can be considered to be close to an asymmetric stretch, while the other would be close to a symmetric stretch. The two other modes would be Raman active. Every copper compound containing the proposed hydroxy bridge shows these absorptions, while copper complexes of 2,2′-bipyridyl without hydroxy bridging fail to show absorption in this region.[14,21] Further, in a hydroxy-bridged complex of chromium the band has shifted to 550 cm.$^{-1}$, indicating that this is a metal-sensitive vibration.[8] The strongest absorption in the 500 cm.$^{-1}$ region is suggested as being due to the asymmetric Cu–O vibration. The weaker vibrations in this region may be associated with the symmetric Cu–O vibration. Cupric oxide also shows absorption in this region.[22] Absorptions in the 500 cm.$^{-1}$ region are also found in basic copper salts.[19] McWhinnie[14] has recently assigned the Cu–O vibration at about 500 cm.$^{-1}$ in related hydroxy-bridged copper compounds. Other weak to medium absorptions are found in the region from 430 to 590 cm.$^{-1}$, and the nature of these is unknown.

Another region of interest is the 260–270 cm.$^{-1}$ region, where a strong band appears in the complexes which is absent in 2,2′-bipyridyl. The band appears to be fairly constant. This band is suggested as the asymmetric Cu–N stretching vibration, and evidence for this assignment is found in recent publications.[11-14,23] The Cu–N vibration for the complex $Cu(bipy)_3(NO_3)_2$ was found at 297 cm.$^{-1}$.[11] In transition metal–amine complexes, where the metal is divalent, the metal–N stretch is found in the 300 cm.$^{-1}$ region.[23] In an investigation of complexes of Cu(II) and heterocyclic bases,[13] the Cu–N vibration was assigned at about 254 cm.$^{-1}$. Similar assignments in the 250 cm.$^{-1}$ region for the Cu–N vibration have been made by McWhinnie.[14] Absorption is also found in the region of 200–240 cm.$^{-1}$, which may be associated with the symmetric Cu–N vibration, since again as in the Cu–O vibration two Cu–N vibrations are expected in the infrared. Table III tabulates the suggested Cu–O and Cu–N assignments made for the various compounds.

The bipyridyl band at about 404 cm.$^{-1}$ shifts to higher frequency upon chelation. Slight shifts are also noted for the 657 and 622 cm.$^{-1}$ bands of 2,2′-bipyridyl.

The bipyridyl complexes are free of absorption from 230 to 170 cm.$^{-1}$, except for the complex $[(bipy)Cu(OH)PF_6]_2 \cdot 2H_2O$, which has absorption in the 200 cm.$^{-1}$ region, and $[(bipy)Cu(OH)]_2SO_4 \cdot 5H_2O$, which has some weak absorptions at <200 cm.$^{-1}$, with the strongest absorption occurring at 192 cm.$^{-1}$. The nature of these bands is not definitely known, although the N–M–N bending vibration should occur in this region and has been reported at 180 cm.$^{-1}$ in related complexes.[13]

Lower frequency bands are also observed at 115 and 150 cm.$^{-1}$. The ligand 2,2′-bipyridyl shows absorptions at 98 and 164 cm.$^{-1}$.

Anion Spectra.—The anion environment in these complexes is of interest. In aqueous solutions the complexes gave molecular conductivities normal for bi-univalent electrolytes.[2] In the solid state it is quite possible that some perturbation of the anions could occur. In Table IV are recorded all of the anion absorptions. In the dipyridyl compounds involving sulfate and perchlorate some lowering of symmetry appears to have taken place, since some splitting of degenerate vibrations and the appearance of forbidden frequencies occurs.[24,25] The complex $[(bipy)Cu(OH)]_2(SCN)_2 \cdot H_2O$ shows C≡N absorption at 2115 and 2080 cm.$^{-1}$ which can be associated with terminal thiocyanate groups.[26-28] For the halide compounds, no conclusive evidence for Cu–halide vibrations could be found.

TABLE IV

ANION ABSORPTIONS IN HYDROXY-BRIDGED COPPER(II) COMPOUNDS (CM.$^{-1}$)

A	1120 (s), 1090 (vs), 1065 (vs), 1030 (s), 618 (vs)
D	1100 (sh), 1080 (vs), 900 (m), 620 (vs), 433 (m)
E	324 (s), 152 (vvw)
G	2115 (w), 2080 (s), 468 (m)
H	830 (vs), 560 (s)
I	1075 (vs), 1043 (vs), 1030 (vs), 620 (vs)
L	1100 (vs), 1058 (s), 1032 (m), 920 (vw), 622 (vs)
N	2117 (m), 2089 (s), 465 (m)

$PtCl_4$ Compound.—In the complex $[(bipy)Cu(OH)]_2$-$PtCl_4 \cdot 3H_2O$ a strong band is observed at 324 cm.$^{-1}$ which is probably the PtCl stretching vibration.

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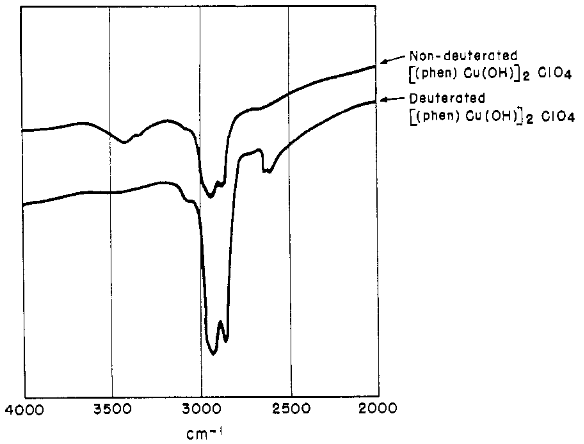

Figure 2.—Comparison of spectra of nondeuterated and deuterated $[(phen)Cu(OH)]_2ClO_4$; Nujol mull spectra.

This band can be assigned to the $\nu_6(E_{2u})$ frequency in the D_{4h} symmetry. For some M_2PtCl_4 salts a strong infrared vibration is found at about 320 cm.$^{-1}$.[29,30] The absorption at 152 cm.$^{-1}$ can be assigned to either ν_7 (E_{2u}) or $\nu_2(A_{2u})$.[29,30]

PF_6 Compound.—In the complex $[(bipy)Cu(OH)PF_6]_2 \cdot 2H_2O$ very strong bands appear at 830 and 560 cm.$^{-1}$ which are probably associated with the PF_6 ion. Additional bands are observed in the 200 cm.$^{-1}$ region, which are not observed in the other complexes. The band at 830 cm.$^{-1}$ can be assigned to the $\nu_3(F_{1u})$ frequency and the 560 cm.$^{-1}$ band to $\nu_4(F_{1u})$ in the O_h symmetry of the PF_6 anion.[31,32] Ebsworth[33] reports infrared bands for PF_6^- at 845 and 559 cm.$^{-1}$.

1,10-Phenanthroline Complexes

OH Vibration.—The positions of the OH stretching in the bridging OH groups in the 1,10-phenanthroline complexes are shown in Table III. It can be observed that the vibration appears in the same region as in the 2,2′-bipyridyl complexes. A comparison of the deuterated and nondeuterated spectra for $[(phen)Cu(OH)ClO_4]_2$ is made in Figure 2. The OH stretching vibration, which is a doublet at about 3400 and 3350 cm.$^{-1}$ in the nondeuterated form, shifts to 2622 and 2600 cm.$^{-1}$ in the deuterated form. This shift is consistent with deuteration of an OH group.

1000–1600 Cm.$^{-1}$ Region.—The spectra in the 1500–1600 cm.$^{-1}$ region differ very little from the unchelated ligand spectra. These results are different from those observed for the 2,2′-bipyridyl complexes. The 1499 cm.$^{-1}$ band in 1,10-phenanthroline appears to shift to higher frequency to 1506–1515 cm.$^{-1}$. A new absorption also occurs on chelation at about 1150 cm.$^{-1}$. In addition, a medium band appears at about 870 cm.$^{-1}$ in the complexes, whereas only a shoulder is present in the ligand itself.

700–800 Cm.$^{-1}$ Region.—Splitting of the out-of-plane OH vibration again occurs in this region, although 1,10-phenanthroline itself shows splitting in the region. The spectra do not change upon chelation for the 1,10-phenanthroline complexes as much as is observed for the 2,2′-bipyridyl complexes. The strongest band in this region for 1,10-phenanthroline is at 734 cm.$^{-1}$. For most of the complexes it is shifted toward lower frequencies to about 720 cm.$^{-1}$. Similar shifts have been observed in related complexes.[7]

Infrared Spectra, 650–70 Cm.$^{-1}$.—As with the 2,2′-bipyridyl complexes several strong bands appear in the 480–500 cm.$^{-1}$ region upon chelation, and the strongest band is suggested as the asymmetric Cu–O stretching vibration in the bridge. The other bands may be associated with the symmetric Cu–O vibration. Also a new, rather constant, band is observed at about 300 cm.$^{-1}$ which is absent in 1,10-phenanthroline, and this is suggested as the asymmetric Cu–N stretching vibration. Table III lists the suggested Cu–O and Cu–N frequencies. The asymmetric Cu–N frequency in the 1,10-phenanthroline complexes appears at higher frequency than that observed for the 2,2′-bipyridyl complexes and might indicate that the Cu–phenanthroline bond is stronger than the Cu–bipyridyl bond. Stability constants for Cu(II)–phenanthroline complexes have been found to be greater than those for Cu(II)–bipyridyl complexes.[34,35] Additional absorption is found in the 250–290 cm.$^{-1}$ regions and might be attributed to the symmetric infrared-active Cu–N stretching vibrations. The 404 cm.$^{-1}$ band in 1,10-phenanthroline shifts to higher frequency to about 430 cm.$^{-1}$ upon chelation. A weak to medium absorption is also observed at about 200 cm.$^{-1}$ which is absent in 1,10-phenanthroline. The N–M–N bending vibration might be expected to occur in this region. The bending vibration of Cu–N has been assigned at about 180 cm.$^{-1}$ in complexes of Cu(II) and heterocyclic bases.[13]

Anion Spectra.—The anion absorptions in the 1,10-phenanthroline complexes are listed in Table IV. Some lowering of symmetry appears also to have occurred in the copper–phenanthroline compounds with sulfate and perchlorate. The thiocyanate ligand appears to exist as a terminal group in these complexes. No conclusive evidence was found for copper–halide vibrations in these compounds.

From the infrared spectra no conclusive evidence was found for coordination of the water in these complexes. The broad absorptions corresponding to the librational modes of coordinated water, such as the rocking motion, wag, and $(Cu-O)H_2$ stretching vibration found at about 875, 535, and 440 cm.$^{-1}$ are not observed.[36] However, the presence of coordinated water cannot be entirely discounted.

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