hydroxyl. The formation of a five-membered ring in the amino acid chelate rather than the seven-membered chelate of the hydroxy acids may be a factor which reinforces this relation. The analogies between the two neutral-region CD spectra are too close, and the differences from the acid-region spectra too great, however, for acceptance of this explanation without at least considering some alternatives.

One alternative possibility, with hydrolyzable metal ion involved, is that hydroxyl binding to the metal ion, in the neutral region, is the differentiating factor. There is too big a gap, however, between the approximate pH of 5 at which the galactonate complex is converted to the strong-CD form and the pH of almost 7 for the alanine complex for this to be the answer. A variant of this might possibly merit more consideration —that the strong-CD forms require binding of two negative charges, in addition to chelation. With the sugar acids, the second negative charge comes with deprotonation of the ligand itself; for the amino acid, the relatively high pH needed to form the chelate would facilitate binding a hydroxyl group to the central ion to give the second charge. Perhaps still another way to consider the amino–hydroxyl difference is in terms of the effect in the acid complex of the protonic charge which is *to be* displaced on going from the acid-region to the neutral-region complex, equating the proton of the hydroxyl group to that on the $-NH_3^+$ group of the amino acid. The possibility of actual deprotonation of the amino group to an imine, to give the analog of the doubly charged sugar acid ligand, seems too remote on chemical grounds but could at least be susceptible to verification by infrared spectral or other techniques. Literature titration investigations of which the author is aware[10,11] are not sufficient to define closely the chemistry in the critical neutral region, and performance of such measurements may be advisable.

The tendency for CD transitions to be split into positive–negative pairs emphasized in prior papers is exhibited here also and still requires theoretical attention.

Acknowledgment.—Great appreciation must be expressed to Dr. W. T. Carnall for directing our attention to Eu(III) and for many helpful discussions.

[10] M. Cefola, A. S. Tompa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, **1**, 290 (1962).

[11] O. E. Zyagintsev and E. V. Goncharov, *Russ. J. Inorg. Chem.*, **8**, 179 (1963).

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The Effect of High Pressure on Internal Vibrations of Nitrogen Heterocyclic Ligands and Their Metal Complexes[1a]

By Richard Bayer[1b] and J. R. Ferraro

Received February 19, 1969

The effect of high pressure on the internal vibrations of pyrazine (1,4-diazine), of 2,2′-bipyridyl, and of some of the metal complexes of these ligands was investigated. Three types of behavior are noted under pressure: (1) all vibrations broaden and decrease in intensity; (2) some doubling of bands occurs; (3) blue shifts are observed. Certain pressure-sensitive vibrations are noted in the ligands and the complexes. The pressure effect on the ligand vibrations is greater than on the vibrations of the complexes.

Introduction

Several early studies of the effects of external pressure on the infrared spectra of various compounds have been made.[2-4] Other studies have since been reported.[5-8] Systematic studies on the effects of external pressure on molecular vibrations in the infrared region of 1600 $\mathrm{cm^{-1}}$ and lower have been neglected. This paper is a preliminary report of a study of the effects of pressure on internal vibrations of two organic ligands and several of their metal complexes in the region 400–1600 $\mathrm{cm^{-1}}$.

Experimental Section

Reagents.—The pyrazine (1,4-diazine) was obtained from Aldrich Chemical Co., Milwaukee, Wis. It had a melting point of 52°, as obtained by a melting point block. The 2,2′-bipyridyl was obtained from Aldrich Chemical Co. and melted at 68°. The complexes used in this work were prepared and reported elsewhere.[9]

Infrared Measurements.—The infrared studies were conducted with an oversized Beckman IR-12 equipped with an 8X beam

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[1] (a) Based on work performed under the auspices of the U. S. Atomic Energy Commision. Presented at the 157th National Meeting of the American Chemical Society Minneapolis, Minn., April 13–18, 1969. (b) At ANL on a Research Participation Program.

[2] (a) E. Fishman and H. G. Drickamer, *Anal. Chem.*, **28**, 804 (1956); (b) A. M. Benson and H. G. Drickamer, *J. Chem. Phys.*, **27**, 1164 (1957); R. R. Wiederkehr and H. G. Drickamer, *ibid.*, **28**, 311 (1958).

[3] C. E. Weir, A. Van Valkenburg, and E. R. Lippincott, *J. Res. Natl. Bur. Std.*, **63A**, 55 (1959).

[4] E. R. Lippincott, F. E. Welsh, and C. E. Weir, *Anal. Chem.*, **33**, 137 (1961).

[5] E. R. Lippincott, C. E. Weir, A. Van Valkenburg, and E. N. Bunting, *Spectrochim. Acta*, **16**, 58 (1960).

[6] J. W. Brasch and R. Jakobsen, *ibid.*, **21**, 1183 (1965).

[7] J. W. Brasch, *J. Chem. Phys.*, **43**, 3473 (1965).

[8] C. Postmus, K. Nakamoto, and J. R. Ferraro, *Inorg. Chem.*, **6**, 2194 (1967).

[9] J. R. Ferraro, J. Zipper, and W. Wozniak, *Appl. Spectry.*, **23**, 160 (1969).

TABLE I

VARIOUS INFRARED SPECTRA OF PYRAZINE (400–1600 CM^{-1})[a]

Lord[12] (molten)	Assignment[13]		Data from this work			
	D_{2h}	Notation	Soln (CS_2)	Molten (52°)	Solid, diamond cell, ambient pressure	Solid, diamond cell, 38 kbars
	B_{2u}	16b			420 s	425 s
			795	793		
804 vs	B_{2u}	11	812	816	804 vs	804 sh
823 vw	B_{1u}	14–6b	860			823 s
926 vvw	B_{1g}	14–16b	920			
1006 w						
1022 m	B_{1u}	12	1022	1022	1029 vs	1029 sh
1032 vw						
1048 vw	B_{1u}	6a + 16b		1048		1044 s
1067 vs	B_{1u}	18a	1065	1065	1067 vs	1080 s
1110 m	B_{1u}	5 + 16b	1104	1107	1118 vvw	
1125 w			1136	1131		
1148 vs	B_{3u}	15	1152	1149	1149 vs	1158 m
1178 m	B_{3u}	10a + 16b	1177	1170		1175 s
1342 m	B_{3u}	14	1355	1365	1355 vvw	1368 vvw
1418 vs	B_{3u}	19b	1414	1415	1422 vs	1438 s
1490 s	B_{1u}	19a	*b*	1484	1497 s	1510 m

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] Interference from CS_2 absorption.

condenser. A description of this apparatus was previously reported.[10] A high-pressure diamond anvil cell was used in these studies.[3,4] Pressure standardizations were made as previously stated.[11]

Discussion and Results

Pyrazine.—Infrared spectra at 400–1600 cm^{-1} are tabluated in Table I. These include a solution spectrum in CS_2, a molten spectrum at 52°, and spectra obtained with the high-pressure diamond cell at ambient and nonambient pressures. For comparison the results of Lord, *et al.*,[12] together with their assignments for pyrazine, are presented. These assignments were based on Langseth and Lord's scheme made for the deuterated benzenes.[13]

Figure 1 shows the spectra at 700–1300 cm^{-1} of pyrazine at ambient and at nonambient pressures. Several of the weak bands observed in Lord's molten spectrum for pyrazine are not seen in the solution, molten, or ambient pressure spectra. When pressure is applied, several additional frequencies are observed in the solid pyrazine spectrum. The 804-cm^{-1} absorption, assigned to a nonplanar hydrogen-bending vibration (notation 11), is observed to shift to 823 cm^{-1}. Only a weak shoulder on this main band remains at 804 cm^{-1}. This weak shoulder may have been present in the ambient pressure spectrum, and may have been obscured by the strong fundamental at 804 cm^{-1}. The different pressure dependencies of these vibrations may have caused them to separate. The 1029-cm^{-1} absorption (notation 12, planar ring vibration) behaves similarly with pressure, a strong band occurring at 1044 cm^{-1} with a shoulder at 1029 cm^{-1}. These bands are also observed in the molten spectrum, but only the lower frequency vibration is found in the solution spectrum. The asymmetrically shaped 1149-cm^{-1} band (notation 15, planar hydrogen bend) in the atmospheric pressure spectrum undergoes a dramatic change with an increase in pressure. At 21 kbars of pressure, two equally intense bands appear at 1158 and 1175 cm^{-1}. These are comparable to bands at 1149 and 1170 cm^{-1} in the molten spectrum and 1152 and 1177 cm^{-1} in the solution spectrum. With increasing pressure, the low-frequency band diminishes in peak intensity relative to the high-frequency band. Blue shifts of bands at 1067, 1355, 1422, and 1497 cm^{-1} also occur with pressure. These bands have been assigned as the planar hydrogen bend (notation 18a) and planar ring fundamentals (notations 14, 19b, and 19a), respectively. A very weak, unassigned peak at 1118 cm^{-1} at ambient pressures is no longer observed with pressure, since both the 1158- and 1080-cm^{-1} bands on either side of the 1118-cm^{-1} band have broadened. The 420-cm^{-1} absorption (notation 16b, nonplanar ring vibration) is only slightly affected by pressure, with a small blue shift occurring.

The following behavior is noted occurring for pyrazine with external pressure.

(1) All bands broaden and diminish in intensity, which is probably associated in part with the pressure gradient existing in the diamond anvil cell used. Such behavior has previously been cited.[3]

(2) Doubling of some bands occurs. This may be due to the separation of accidentally overlapping bands, probably caused by the different pressure dependencies manifested by the two vibrations. Alternatively, some doubling of bands may be induced by pressure, because of a lowering of the symmetry of the molecule. Another possible explanation is that the ligand molecules are in various states of crystal environment under pressure and this may cause the splitting.

(3) Relatively minor blue shifts occur. This too

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(10) L. J. Basile, C. Postmus, and J. R. Ferraro, *Spectry. Letters*, **1**, 189 (1968).

(11) J. R. Ferraro, S. S. Mitra, and C. Postmus, *Phys. Rev. Letters*, **18**, 455 (1967).

(12) R. C. Lord, A. L. Marston, and F. A. Miller, *Spectrochim. Acta*, **9**, 113 (1957).

(13) A. Langseth and R. C. Lord, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **16**, No. 6, 1 (1938).

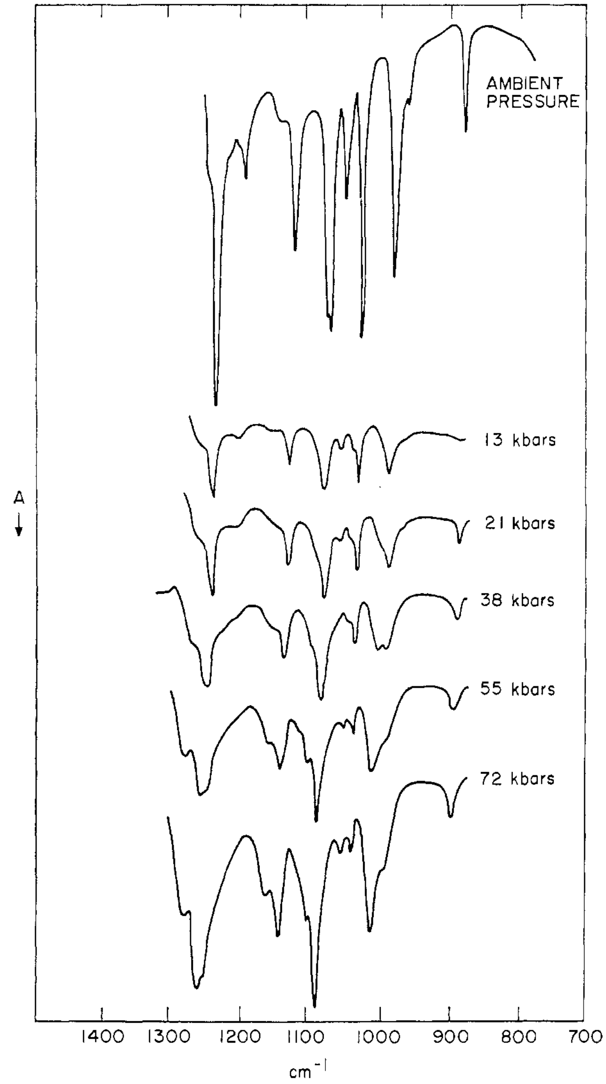

Figure 1.—Spectra of pyrazine at various pressures.

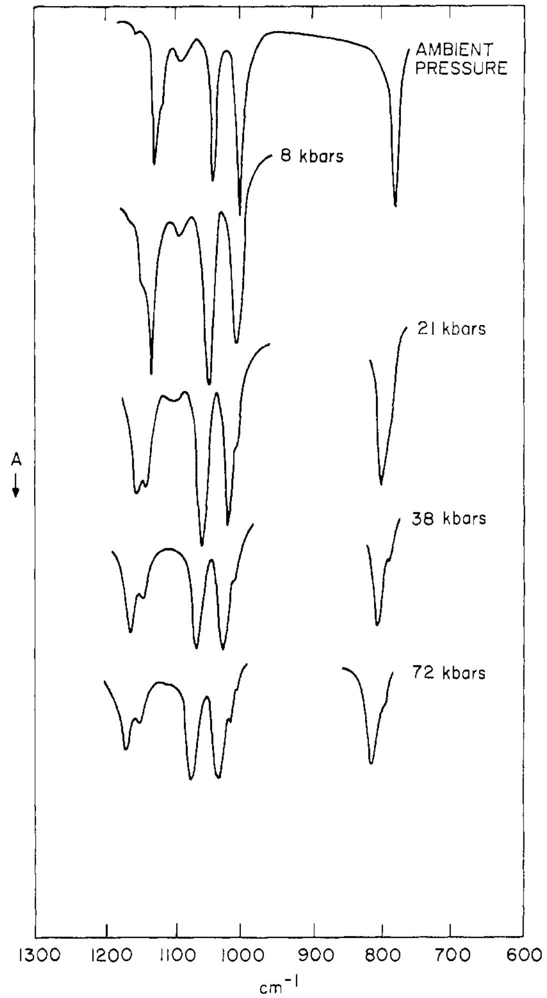

Figure 2.—Spectra of 2,2′-bipyridyl at various pressures.

has been previously observed,[2,3] although no explanation has been offered heretofore. The lowering of intermolecular distances occurring with an increase in pressure[3-8] makes certain vibrations more difficult to occur. Consequently, additional energy is required for the particular mode.

Certain similarities are noted in the pressure spectrum of pyrazine with the molten and solution spectra. However, the solution spectrum is observed to induce only some of the changes seen for the molten and pressure spectra. Additionally, certain modes involving planar and nonplanar vibrations are sensitive to pressure. Some of these modes involve an increase in molecular volume.

Pyrazine Complexes.—Table II compares infrared data at 700–1500 cm^{-1} for the pyrazine ligand and several pyrazine complexes.[9] In general, bands are shifted to higher frequencies upon complexation, the 804- and 1497-cm^{-1} bands being exceptions. There is a marked similarity in the effects of pressure on the spectrum of the uncomplexed pyrazine with that of the spectra of the complexes (at ambient pressures). The ligand spectrum at ambient pressure shows a single band in the 800-, 1030- and 1150-cm^{-1} regions. With pressure two bands appear in these regions, similar to the results obtained for the complexes at ambient pressure. The nature of these vibrations in the complexes is unknown, but these have been assigned in the ligand (notations 11, 12, and 15). The 1422-cm^{-1} band (notation 19b), which shows only a blue shift with pressure in the ligand, is observed to split into two bands upon complexation. Thus, it would appear that application of external pressure on a ligand simulates complexation. Further, the complexation process itself may be considered to be a form of pressure reaction, since certain constraints and restraints are placed on the ligand because of the polymeric environment it finds around itself. Thus, it is not too surprising to note these similarities.

External pressures applied on Co(pz)Cl$_2$ (pz = pyrazine) show only minor effects (Table III), the largest effect being noted with the 1172-cm^{-1} vibration. At the lowest applied pressure a new band appears at 1185 cm^{-1} of almost equal intensity as the 1172-cm^{-1} band. With an increase in pressure the 1172-cm^{-1} band decreases in intensity and becomes very weak, while the 1185-cm^{-1} band increases in intensity and shifts to 1206 cm^{-1}. The 1365- and 1490-cm^{-1} bands show only slight blue shifts with pressure. The 1422-cm^{-1}

TABLE II

INFRARED SPECTRA OF PYRAZINE AND SEVERAL PYRAZINE COMPLEXES (CM^{-1})

Pyrazine							
Diamond cell, ambient pressure	Diamond cell, 38 kbars	$Fe(pz)_2Br_2$[a]	$Mn(pz)_2Br_2$	$Fe(pz)_2Cl_2$	$Cu(pz)_2Cl_2$	$Ni(pz)Br_2$	$Co(pz)Br_2$
		KBr spectra,[9] ambient pressures					
			788	788	797	788	785
804 vs	804 sh	808	805	805	802	815	810
	823 s	815	812	812	818	823	818
				818			
		988	988	985	990	980	987
1029 vs	1029 sh						
	1044 s	1050	1050	1050			1055
1067 vs					1067		
	1080 s	1088	1084	1085	1092	1096	1087
1118 vvw		1120	1120	1114	1115	1117	1118
				1118			
1149 vs							
	1158 m	1155	1155	1154		1155	1152
	1175 s	1160	1160	1163	1168	1192	1164
			1206				
1355 vvw							
	1368 vvw			1398	1365	1368	1365
						1392	1390
1422 vs		1415					
	1438 s	1420	1422	1415	1415	1410	1412
				1422	1422	1422	1418
1497 s		1488	1488	1485			
	1510 m				1487	1488	

[a] pz = pyrazine.

TABLE III

EFFECT OF PRESSURE ON $Co(pz)Cl_2$ (CM^{-1})

Diamond cell, ambient pressure	Diamond cell, 72 kbars	Diamond cell, ambient pressure	Diamond cell, 72 kbars
795 vs	805 vs	1172 s	1170 sh
	908 vw		1206 m
1030 vvw		1365 w	1370 w
1060 vs	1060 vs	1422 vs	1430 vs
1092 vvw			1439 sh
1122 vs	1110 sh	1490 s	1494 vs
	1130 vs		

TABLE IV

EFFECTS OF PRESSURE ON 2,2′-BIPYRIDYL (400–1500 CM^{-1})

Assignments[a]	Diamond cell, ambient pressure	Diamond cell, 55 kbars
8a	1585 vs	1602 vs
8b	1565 vs	1583 vs
	1544 vvw	1544 vvw
	1525 vvw	1525 vvw
	1510 vvw	1510 vvw
	1492 vvw	1492 vvs
19a	1462 vvs	1465 vvs
19b	1420 vvs	1420 vvs
	1270 sh	1275 sh
3	1253 vs	1267 m, 1253 sh
9a	1215 w	Disappears
	1170 vw	1168 w
15	1142 s	1149 m
	1092 s	1110 w
18a, b	1088 s	1097 s
	1068 m	1068 vvw
12	1043 s	1042 vvw
1	998 s	1015 m, 998 sh
	978 sh	
10a	895 m	898 vw
	834 vvw	
10b	762 vvs	766 vvs
11	742 w	742 w
	658 m	660 m
6a	622 w	628 w
16b	405 m	405 vw

[a] A. I. Popov, J. C. Marshall, F. B. Stute, and W. B. Person, *J. Am. Chem. Soc.*, **83**, 3586 (1961); J. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, Jr., and A. J. Wilson, *Spectrochim. Acta*, **23A**, 1121 (1967).

band separates into two bands at 1430 and 1439 cm^{-1}. The latter bands involve vibrations 14, 19a, 19b, respectively. Several of the vibrations found to be pressure sensitive in the ligand are also pressure sensitive in the complex.

2,2′-Bipyridyl.—The spectral absorptions of 2,2′-bipyridyl at ambient pressure and at 55 kbars are tabulated in Table IV. The assignments, which are also included in the table, are those of Popov, *et al.*[14] Figure 2 illustrates the spectra at 700–1400 cm^{-1} at various pressures. The following major changes are observed with pressure: (1) The 405-cm^{-1} absorption which is assigned as a nonplanar ring vibration (notation 16b) is drastically reduced in intensity. (2) The 998-cm^{-1} absorption, which has been assigned as a planar ring vibration (notation 1), is replaced by a medium band at 1015 cm^{-1} and a shoulder remains at 998 cm^{-1}. (3) Two very weak bands are observed at 1068 and 1042 cm^{-1} in place of the strong 1043-cm^{-1} band (planar ring vibration, notation 12). (4) Blue shifts are observed with vibrations at 18a, 18b, 15, 8a, and 8b. (5) The 1253-cm^{-1} band (notation 3) is replaced by two bands at 1267 and 1253 cm^{-1}. (6) Vibration 9a disappears (1210 cm^{-1}). Small blue shifts are also observed with some of the other vibrations.

Table V summarizes pressure-sensitive vibrations found in pyrazine and 2,2′-bipyridyl. It can be ob-

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[14] A. I. Popov, J. C. Marshall, F. B. Stute, and W. B. Person, *J. Am. Chem. Soc.*, **83**, 3586 (1961).

TABLE V

SUMMARY OF PRESSURE SENSITIVE VIBRATIONS IN PYRAZINE AND 2,2′-BIPYRIDYL

Pressure-sensitive vibrations[a]		Notation of vibration	Schematic diagram[b]	Notation of vibration	Schematic diagram[b]
Pyrazine	11, *12*, *15;* separate into 2	1	Ring	12	Ring
	bands	3	H bend	14	Ring
	14, *16b*, *18a*, *19a*, 19b;	6a	Ring	15	H bend
	blue shifts	8a	Ring	16b	Ring
Bipyridyl	1, 3, *12;* separate into 2	8b	Ring	18a	H bend
	bands	9a	H bend	18b	H bend
	8a, 8b, *15*, *18a*, *b*, *16b*, *19a*, 10a,	10a	H bend	19a	Ring
	10b, 6a; blue shifts	10b	H bend	19b	Ring
	9a; disappears	11	H bend		

[a] Pressure-sensitive vibrations common to both ligands are italic. [b] This is a schematic description of each vibration corresponding to the notations used in ref 12 and 13.

TABLE VI

COMPARISON OF SPECTRUM OF 2,2′-BIPYRIDYL WITH THE SPECTRA OF THE BIPYRIDYL COMPLEXES OF Eu, Ni, AND Co (CM^{-1})

2,2′bipyridyl, diamond cell, 55 kbars	Eu(bipy)$_2$Cl$_3$,[a,b] diamond cell	Ni-(bipy)$_3$Cl$_2$[c]	Co-(bipy)$_3$Cl$_2$[c]
	Ambient pressure		
1602 vs	1602 vvs	1602	1600
1583 vs	1578 vs	1571	1570
1544, 1525, 1510 vvw	1541, 1510 vvs		
1492 vvw	1498 s	1492	1490
1465 vvs	1480 s	1473	1470
1420 vvs	1442 vs	1443	1442
	1320 s	1385	
		1315	1312
1275 sh		1285	1284
1267 m	1270 w	1250	1249
1253 sh	1245 s		
	1218 s	1230	1230
1168 w	1170 s	1180	1179
1149 m	1158 vs	1160	1160
1110 w	1109 s	1102	1100
1097 s			
1068 vvw	1068 s	1063	1063
1042 vvw	1049 w	1043	1043
1015 m	1015 vs	1020	1018
998 sh	980 w		
898 vw	900 vw	910	908
	815 m		
766 vvs	771 vs	778	778
742 w	740 s	765	765
	710 s	738	737
660 m	650 s	655	651
628 w	629 s	635	630
	595 sh		
	548 s		
405 vw	425 w		

[a] bipy = 2,2′-bipyridyl. [b] L. J. Basile, D. L. Gronert, and J. R. Ferraro, *Spectrochim. Acta*, **24A,** 707 (1968). [c] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2213 (1931).

served that certain vibrations are pressure sensitive for both ligands. The lack of a center of symmetry for 2,2′-bipyridyl allows additional vibrations to appear, which are not allowed in the infrared spectrum of pyrazine. For example, vibrations 1, 3, 6a, 8a, 8b, 9a, 10a, and 10b are only Raman active in pyrazine. Thus, excluding these infrared-silent vibrations (in pyrazine only), the number of pressure sensitive vibrations that are common to both ligands is striking. In some of these modes a large change in volume is involved with the particular vibration, and it is these modes that are particularly pressure sensitive.

Complexes of 2,2′-Bipyridyl.—Table VI presents a comparison of the spectrum of 2,2′-bipyridyl under pressure with that of several complexes measured at amibent pressure. When external pressure is applied to the ligand, a spectrum is obtained which has marked similarity in peak positions with the ambient pressure spectra of the Eu(bipy)$_2$Cl$_3$ complex. These results are similar to those obtained for pyrazine. The similarities with the Ni(bipy)$_3$Cl$_2$ and Co(bipy)$_3$Cl$_2$ complexes are also to be noted. For example, the ligand band at 1253 cm^{-1} in the ambient pressure experiment of 2,2′-bipyridyl separates into two bands at 1267 and 1253 cm^{-1} under pressure. The complex Eu(bipy)$_2$Cl$_3$ also shows two bands in this region. Similar results are obtained for the 1043- and the 998-cm^{-1} ligand bands. Subjecting Eu(bipy)$_2$Cl$_3$ to pressures, as in the case of Co(pz)Cl$_2$, produces only minor changes. Table VII summarizes these results.

TABLE VII

SUMMARY OF RESULTS OF PRESSURE STUDIES OF Eu(bipy)$_2$Cl$_3$ (CM^{-1})

Diamond cell, ambient pressure	Diamond cell, 72 kbars	Diamond cell, ambient pressure	Diamond cell, 72 kbars
1602 vvs	1605 s	1109 s	1112 m
1578 vs	1585 sh	1068 s	1087 w
1541 vvw	1542 w	1049 w	Disappears
1510 vvw	1510 m	1015 vs	1020 s
1498 s	1498 sh	980 w	980 vw
1480 s	1485 m	900 vw	900 vw
1442 vs	1445 s	815 m	815 m
1320 s	1340 sh	771 vs	775 s
	1325 m	740 s	740 s
1270 w	1260 m	710 s	720 sh
1245 s	1250 m	650 s	650 s
1218 s	Disappears	629 s	633 m
1170 s	1170 m	595 sh	
1158 vs	1158 m	548 s	Reduced in intensity
	1150 m	425 m	425 m

Conclusions

The preliminary results obtained in this study appear to indicate the following information: (1) Certain pressure-sensitive internal vibrations in the ligand molecule are also pressure sensitive in the complex. (2) Pressure effects on the ligand vibrations are greater than those measured on the complexes. (3) The pressure effect on the ligands appears to give a spectrum similar to that of the complex. (4) Three types of behavior are noted for internal vibrations under pressure: (a) broadening and diminishing in intensity; (b) doubling of bands; (c) blue shifts of bands.

Further studies are under way with other ligand systems to determine to what extent the above conclusions are general. The necessity to study a ligand whose vibrations are properly assigned limits the choices that one can make for these studies.

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Metal Derivatives of Arylazopyrazolone Compounds. VIII. Molarity Quotients of the Sulfonic Acid Derivatives of Azo-3- and Azo-5-pyrazolones

BY FRED A. SNAVELY AND DWIGHT A. SWEIGART[1]

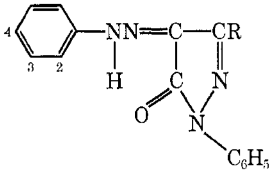
Received May 15, 1968

The formation constants of divalent metal ions with sulfonic acid derivatives of benzeneazo-3- and benzeneazo-5-pyrazolone have been measured in 75 vol % dioxane. With the sulfonic acid group in the chelate position (*ortho* to the azo linkage), the ligands are terdentate, and 1:1 complexes are formed. The decreasing order of stability for the divalent metal derivatives of 5-methyl-1-phenyl-4-(2-sulfophenylazo)-3-pyrazolone is Cu > UO_2 > Ni > Co > Zn > Cd > Mg > Ca > Sr > Ba. The *m*- and *p*-sulfo-substituted azo compounds behave like other bidentate azopyrazolone derivatives and form 2:1 compounds.

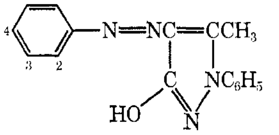
Introduction

Arylazo compounds which contain acidic or basic groups in one or more of the *ortho* positions are strong coordinating ligands.[2] In the dye industry such molecules generally contain one or more sulfonic acid groups which act as solubilizing centers. Drew[3] and coworkers have prepared metal derivatives with a few of the sulfonic acid compounds. Shetty[4] has stated that a sulfonic acid group in the chelate position *ortho* to a hydroxy group in *o,o'*-dihydroxyazo compounds causes dyes to be difficultly water soluble and difficult to chrome. He suggested that the sulfonic acid group is involved in the coordination although not directly attached to the metal ion. However, no work has been reported on azo compounds which contain sulfonic acid groups *ortho* to the azo linkage.

We have prepared and studied the chelating ability of a series of azo-3- and azo-5-pyrazolones which contain sulfonic acid groups in either the 2 or 4 position.



I, R = CH_3
II, R = $COOC_2H_5$



III

Experimental Section

Preparation of Azo Compounds.—The azo derivatives were prepared by coupling the appropriate diazotized amines to the pyrazolones in aqueous solution containing enough sodium hydroxide to dissolve the pyrazolones and sodium carbonate to serve as a buffer. The coupling bath was just neutralized with hydrochloric acid, and the crude product was isolated as the sodium salt of the sulfonic acid group. The III-3-SO_3H and the III-4-SO_3H were isolated as the free acids. The sodium salts and the free acids were recrystallized from 50% ethanol and dried in an oven at 110°. Purity was determined by measuring the neutral equivalents which gave values within 0.2% of those calculated.

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.[5] The solutions were so adjusted that in 100 ml of solution there were 0.9568 mmol of azo compound, 0.9568 mmol of nitric acid, and 0.200 mmol of metal nitrate. The solution of the azo compound was thus equivalent to the free sulfonic acid. To those compounds which had been isolated as the free acid, no nitric acid was added, but 0.9568 mmol of sodium nitrate was added. A 1.0405 *N* solution of carbonate-free sodium hydroxide was used. The meter reading correction factor (log U_H)[6] was 0.47 for the calculation of the first acid dissociation constant and 0.41 for the calculation of the formation constants and the second dissociation constant. The acid dissociation constants of the chelating agents were obtained by titrating the azo compound in the absence of divalent metal ions.

Calculations.—The stability constants were calculated by curve fitting[7] by the method of least-squares using an IBM 1130 computer (eq 1). β_n is the product of the first n stability con-

$$-\beta_1 + \frac{(\bar{n} - 2)a}{1 - \bar{n}}\beta_2 + \frac{\bar{n}}{(1 - \bar{n})a} = 0 \qquad (1)$$

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