

INFRA-RED SPECTRA OF 1:10-PHENANTHROLINE METAL COMPLEXES IN THE ROCK SALT REGION BELOW 2000 cm^{-1}

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(Received 9 September 1958)

Abstract—Infra-red spectra of twenty two metal-1:10-phenanthroline perchlorates together with spectra of the free ligand, its hydrate and perchlorate salt have been obtained in the region between 600 and 2000 cm^{-1} from Nujol mulls. In general, the spectra of the complexes were remarkably similar in their gross features and no obvious correlations with magnetic or other physical properties were noted. However, the results provide evidence for co-ordination in the case of the alkali metal complexes and also indicate a co-ordination number of eight in the alkaline earth, lead and manganese complexes. The compositions of all compounds studied were confirmed by elementary microanalysis and the list includes several new compounds as well as a few having compositions differing slightly from those previously reported. The interpretation of the principal features of the spectra is discussed.

ALTHOUGH an increasing number of papers reporting on the infra-red spectra of metal co-ordination complexes have appeared in the recent literature, the results available are not yet adequate for a proper assessment of this technique's value, apart from its usefulness in characterization and identification. Most of the studies which have appeared to date have dealt with complexes involving either very simple ligands such as NH_3 or CN^- ,⁽¹⁻⁴⁾ or with ligands having a co-ordinating group which can be associated with a characteristic vibration frequency such as β -diketones⁽⁵⁾ or compounds containing $-\text{COOH}$ or $-\text{NH}_2$ groups.⁽⁶⁻⁸⁾ Very few data have been presented for compounds where the complexing agent is a fairly large and complicated molecule. In general, more or less marked alterations in the spectrum of the ligand have been reported to occur upon co-ordination, and in some cases it has been possible to interpret these changes satisfactorily in terms of the structure or geometry of the complex, or to relate them to changes in bonding in the ligand. It has also been found that these changes in the ligand spectrum are relatively insensitive to the nature of the metal involved such that disappointingly little has been learned about the metal to ligand bond.

In the present work, the infra-red spectra of a number of heavy metal complexes with 1:10-phenanthroline have been obtained together with the spectra of several alkali and alkaline earth complexes, acid salts and the hydrate. For comparison purposes, the spectra of a small number of 2:2-bipyridine complexes were also

⁽¹⁾ D. B. POWELL and N. SHEPPARD, *J. Chem. Soc.* 3108 (1956).

⁽²⁾ G. M. BARROW, R. H. KRUEGER and F. BASOLO, *J. Inorg. Nucl. Chem.* 2, 340 (1956).

⁽³⁾ L. H. JONES, *J. Chem. Phys.* 26, 1578 (1956); 27, 468, 665 (1957).

⁽⁴⁾ G. F. SVATOS, D. M. SWEENEY, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* 79, 3313 (1957).

⁽⁵⁾ H. F. HOLTZCLAW and J. P. COLLMAN, *J. Amer. Chem. Soc.* 79, 3318 (1957).

⁽⁶⁾ M. L. MORRIS and D. H. BUSCH, *J. Amer. Chem. Soc.* 78, 5178 (1956).

⁽⁷⁾ R. B. PENLAND, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* 79, 1575 (1957).

⁽⁸⁾ K. NAKAMOTO, J. FUJITA, S. TANAKA and M. KOBAYASHI, *J. Amer. Chem. Soc.* 79, 4904 (1957).

obtained. The anion present in all cases was perchlorate which was selected because it gave nicely crystalline salts which could be easily handled. Since many complexes of 1:10-phenanthroline have not been completely characterized, or doubtful points are present in the literature preparations, all compounds were subjected to elemental microanalysis before their spectra were accepted. In several cases, the compositions determined by the analytical data represented new compounds or minor variations from the compounds previously reported.

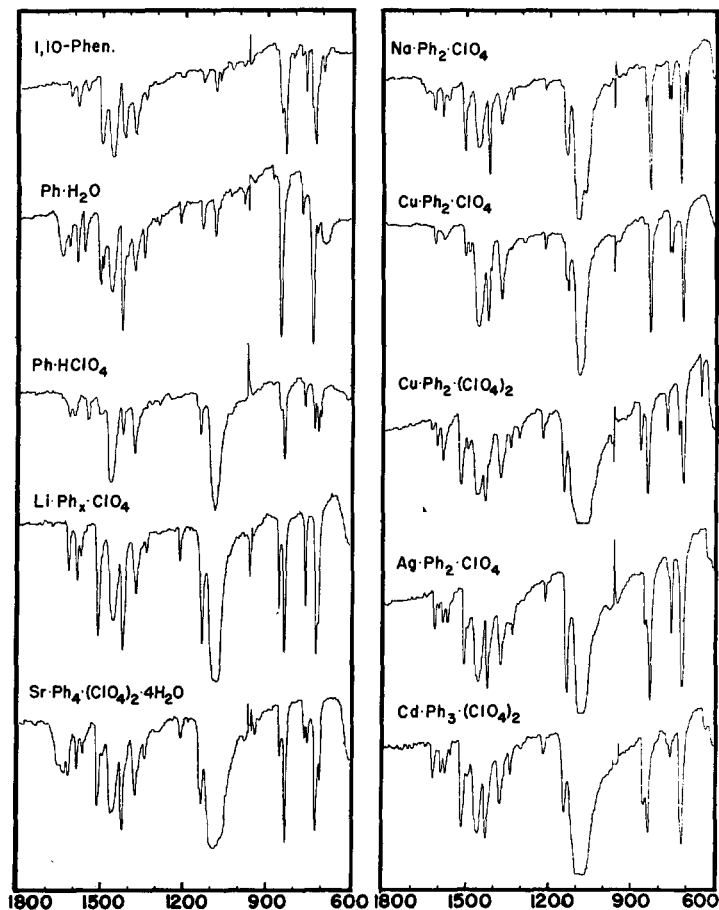


FIG. 1.—Infra-red spectra of 1:10-phenanthroline and its hydrate, perchlorate and some of its metal complexes as Nujol mulls.

The spectral results are of interest in connexion with questions regarding the metal co-ordination number in certain complexes and also provide a limited amount of information regarding bonding in the complexes.

EXPERIMENTAL RESULTS

Spectra of the 1:10-phenanthroline metal complexes, the spectrum of the free base, its hydrate and perchlorate salt are shown in Figs. 1-3 while the measured frequencies of the band maxima are given in Table 1. Similar information for the bipyridine complexes is given in Table 2 and selected spectra are shown in Fig. 3.

Inspection of the results shows that in their gross features, the spectra of the various phenanthroline complexes are remarkably similar in appearance and show no obvious correlations either with magnetic or other physical properties of the complexes, with the valence of the metal or with the number of ligand groups co-ordinated. Since the vibrational frequencies observed in the rock salt region arise exclusively in the ligand part of the complex, which, in this case, is fairly large and complex, it is perhaps not surprising that the spectra do not vary markedly from metal to metal.

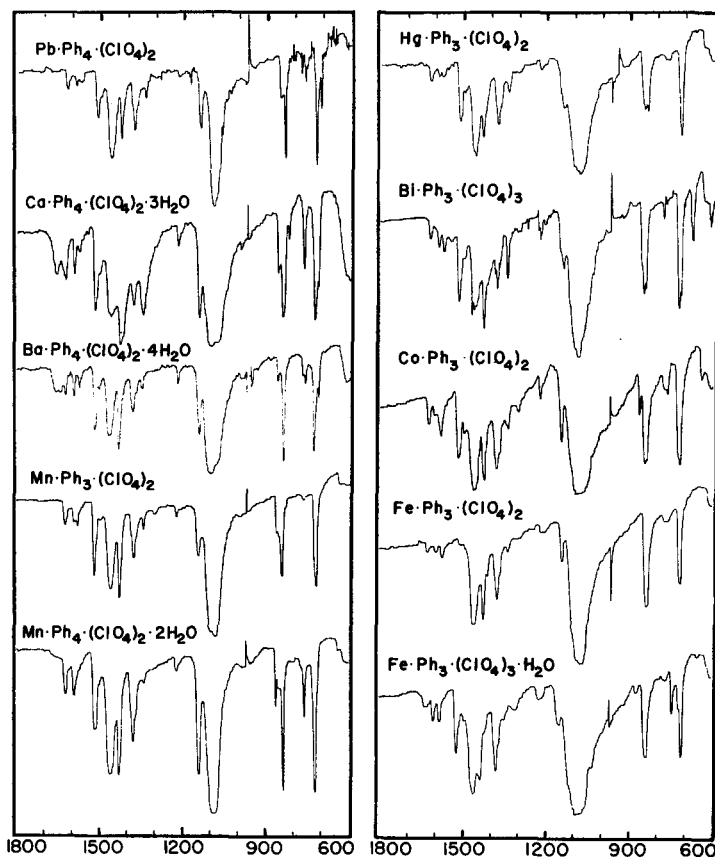


FIG. 2.—Infra-red spectra of some metal complexes of 1:10-phenanthroline from Nujol mulls.

Similar observations have been made elsewhere in studies involving simpler ligands.

More detailed examination of the spectra shows that the metal complexes are easily distinguishable from either the free base, the hydrate or the acid salt and this provides a satisfactory method of detecting the presence of occluded or uncomplexed ligand. For example, phenanthroline perchlorate can be identified in mixtures by a strong band at 1544 cm^{-1} since the corresponding band in the metal complexes is confined to the range between 1510 and 1530 cm^{-1} . Several other acid salts were also examined in the course of this investigation including the chloride, bromide, nitrate and sulphate. In all cases the band mentioned fell consistently outside the range of the same band in the metal complexes. Differentiation of the free base or the hydrate from the metal complexes requires more careful comparison since no single band

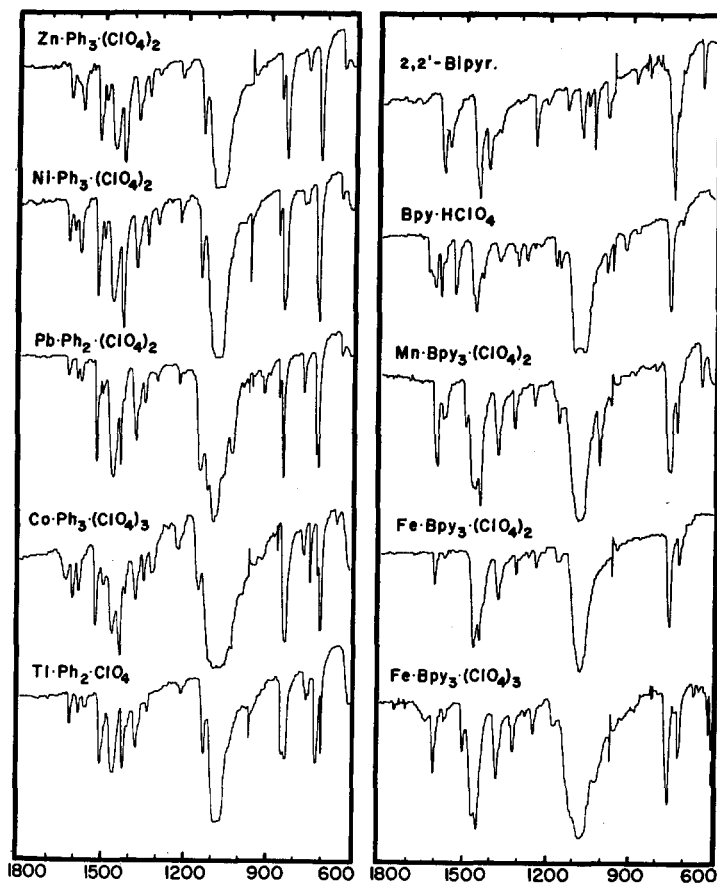


FIG. 3.—Infra-red spectra of some metal complexes of 1:10-phenanthroline and 2:2'-bipyridine from Nujol mulls.

can be selected which will give an unequivocal answer as in the case of the acid salts. Detailed comparison of the bands in the $700\text{--}900\text{ cm}^{-1}$ region appears most suitable.

The spectra of the metal complexes themselves differed in minor respects such that no two were identical, although the cobalt and nickel were nearly so. Principal differences occurred in the $700\text{--}900\text{ cm}^{-1}$ region and consisted of varied patterns in the splitting of the strong bands near 720 and 850 cm^{-1} .

The results for the Li, Na and alkaline earth complexes are of some interest in view of questions raised⁽⁹⁾ as to whether the alkali metals actually are chelated in the complexes, and in regard to the high co-ordination number observed for the alkaline earths. Since experimental limitations prevented study of the spectral region in which frequencies associated with the metal-nitrogen bond might be expected, the evidence bearing on these two questions is somewhat indirect. However, in the case of the heavy transition metal complexes, certain modifications of the spectrum of the free ligand occurred which appear to be characteristic of the ligand in the bound state. Perhaps the most obvious of the alterations was a general shift of the ring vibrations in the $1400\text{--}1600\text{ cm}^{-1}$ region to higher frequency. These modifications were clearly present

⁽⁹⁾ W. W. BRANDT, F. P. DWYER and E. C. GYARFAS, *Chem. Rev.* **54**, 959 (1954).

TABLE 1.—INFRA-RED FREQUENCIES OF METAL 1:10-PHENANTHROLINE PERCHLORATES IN THE NaCl REGION BELOW 2000 cm⁻¹

P ⁺	PH ₂ O	PHClO ₄	LiP [†]	NaP ₂	CaP ₄ [†]	SrP ₄	BaP ₄	MnP ₄	MnP ₃	FeP ₃	FeP ₂	CoP ₃	CoP ₂	NiP ₃	CuP ₂	CuP ₃	AgP ₂	ZnP ₃	CdP ₃	HgP ₃	TlP ₂	PbP ₄	PbP ₂	PbP ₃	
704	612	610	613	718	714	712	611	610	613	610	610	613	610	610	610	612	610	612	611	611	613	612	608	614	
722	707	713	725	724	724	724	640	645	714	719	607	714	607	647	632	647	720	645	640	611	710	667	667	633	
734*	738*	731*	730*	729*	729*	729*	724*	724*	724*	724*	721*	717*	721*	723*	718*	726*	726*	726*	722*	722*	723*	729*	720*	728*	
744	766	766	770	760	760	760	727	729	726	747	760	736	735	738	735	737*	736	737*	737*	729	729	772	772	771	
767	777	777	824	771	771	770	731	766	753	765	768	778	768	779	777	767	764	770	767	767	760	767	772	781	
783	845	845	830	824	824	824	775	777	780	775	778	796	778	779	777	778	777	778	778	777	778	778	786	786	
813	847*	850*	843*	845*	839*	838*	848*	846*	844*	849*	838*	847*	849*	848*	847*	848*	840*	840*	848*	843*	843*	842*	847*	854*	
842*	855	855	862	861	861	861	858	849	878	849	838	884	838	848	847*	840*	840*	848*	843*	843*	855	847*	854*	862	
	884	884	892	892	892	892	867	869	869	869	863	884	863	869	862	850	850	850	853	853	853	859	862	890	
	889	889	911	859	859	859	867	869	869	869	863	884	863	869	862	850	850	850	853	853	853	859	862	930	
	931	931	874	861	861	861	867	869	869	869	863	884	863	869	862	850	850	850	853	853	853	859	862	930	
854	1033	994	992	950	950	950	865	1035	1039	1039	994	1039	994	869	930	930	961	930	933	934	934	938	938	1008	
	1080	887	992	950	950	950	865	1035	1039	1039	994	1039	994	869	930	930	961	930	933	934	934	938	938	1008	
876																									
993																									
1029																									
1075																									
1092	1093	1088*	1088*	1090*	1103*	1100*	1090*	1085*	1086*	1085*	1095*	1085*	1095*	1085*	1090*	1090*	1090*	1090*	1080*	1083*	1080*	1090*	1090*	1100*	
	1139	1145	1145*	1144	1143	1141	1148	1147	1149	1147	1146	1148	1146	1148	1150	1148	1143*	1148	1147	1147	1148	1137	1145	1143	
	1142	1158	1220	1150	1150	1150	1217	1208	1213	1212	1222	1224	1222	1224	1222	1222	1222	1222	1227	1227	1220	1220	1210	1151	
	1219	1228	1223	1217	1217	1218	1226	1223	1225	1224	1228	1224	1222	1224	1222	1227	1222	1222	1227	1228	1229	1220	1302	1207	
1137	1297	1287	1257	1221	1217	1218	1306	1315	1305	1305	1298	1231	1298	1305	1315	1309	1310	1344	1344	1344	1344	1342	1345	1223	
1217	1349	1320	1342	1347	1347	1348	1345	1342	1342	1342	1341	1342	1341	1341	1345	1344	1350	1344	1344	1344	1344	1342	1345	1306	
1346																									
	1410	1419	1413*	1430*	1431*	1430*	1431*	1433*	1430*	1433*	1428*	1439*	1428*	1439*	1425	1425	1433*	1433*	1433*	1433*	1436*	1429*	1435	1431*	
1423*	1427*	1428	1426	1500	1498	1498	1499	1497	1499	1499	1496	1499	1496	1499	1499	1499	1500	1500	1501	1502	1502	1500	1500	1431*	
	1497*	1502	1503	1518*	1518*	1516*	1520*	1515	1522*	1522*	1510	1522*	1510	1522*	1525*	1525*	1515*	1522*	1519	1518*	1518*	1515	1515	1520	
1505*	1508*	1544*	1513*	1518*	1518*	1516*	1519*	1515	1522*	1522*	1510	1522*	1510	1522*	1525*	1525*	1515*	1522*	1519	1518*	1518*	1515	1515	1520	
1558	1565	1571	1572	1575	1572	1570	1581	1585	1583	1583	1584	1585	1584	1584	1584	1584	1584	1584	1584	1584	1584	1584	1584	1550	
1591	1590	1599	1591	1592	1593	1592	1592	1602	1605	1605	1606	1610	1606	1606	1610	1609	1609	1609	1609	1609	1609	1609	1609	1550	
1615	1618	1618	1623	1622	1624	1624	1624	1632	1633	1633	1626	1638	1626	1626	1629	1629	1629	1629	1629	1629	1629	1629	1629	1575	
	1645	1635	1658	1658	1642	1640	1622	1632	1633	1633	1626	1638	1626	1626	1629	1629	1629	1629	1629	1629	1629	1629	1629	1629	1593
																									1624
																									1624

* Indicates the more intense bands.
 † See Experimental section for analytical results.
 ‡ P = 1:10-phenanthroline. See Experimental section for complete formulae of salts.

TABLE 2.—INFRA-RED FREQUENCIES OF SOME METAL 2:2'-BIPYRIDINE PERCHLORATES IN THE NaCl REGION BELOW 2000 cm^{-1}

B†	BHClO ₄	Mn ^{II} B ₃	Fe ^{II} B ₃	Fe ^{III} B ₃	Co ^{II} B ₃	Co ^{III} B ₃	Ni ^{II} B ₃
652		650		669	652		650
	722	720	720	722		720	717
739		736	728	726	735	724	732
				741			
755*	763*	762*	763*	764*	766*	763*	763*
		767	768	797	774	792	771
892	888	810		889	889	889	886
	926		954	932			927
992	994	973	997		964		961
	1020			1020	1021		1005
1041	1042	1007		1030	1045	1036	1016
1065	1050						1021
		1018	1070		1072		
		1045					
1085	1070*	1088*	1084*	1080*	1085*	1088*	1083*
1090							
	1112						
1140	1161	1161	1160	1170	1158	1166	1156
	1177	1175	1167	1180	1172	1177	1169
	1234				1218		1217
1252	1253	1247	1242	1247	1248	1246	1246
	1281		1272	1278			
	1312		1315		1317		1313
	1324	1320		1321		1320	
				1370			
1421*	1370	1446*	1448*	1456*	1446*	1455*	1445*
					1474		
		1496		1503	1498		1496
	1537*					1505	
1560	1576	1570	1569	1567	1566	1570	1564
1583*	1589	1576			1576		1574
	1610	1601*	1607	1608	1604*	1609	1603*
	1622			1630			
	1633	1608					

* Indicates the more intense bands.

† B = 2:2'-bipyridine. See Experimental section for complete formulae of salts.

in both the lithium and sodium complexes as well as those of the alkaline earths, although the magnitude of the shifts was not as great as for the heavy metals. Since no bands attributable to the free base or its hydrate were observed, one is led to conclude that all the phenanthroline present in these light metal complexes is co-ordinated. This conclusion is supported by the observation that no ligand was lost when the compounds were heated *in vacuo* at 110°C. The analytical data confirm the presence of four (bidentate) ligands in the strontium and barium complexes and between three and four for calcium. Similarly, the spectral and analytical data support a co-ordination number of eight for manganese(II) and lead(II) in their tetrakis complexes.

However, the spectra of literature preparations with tin(II) give no evidence of co-ordination and showed only the lines of phenanthroline perchlorate.

Co-ordination involving protons, either in water or from an acid, produced the same characteristic shifts as co-ordination to a metal. In the case of water, the magnitude of the effects was small, smaller even than for the alkali and alkaline earth metals, but in the salts of strong acids where the proton is bound firmly to the nitrogen atom, the shifts were quite striking.

DISCUSSION OF THE SPECTRAL RESULTS

No general, systematic study of the vibrational frequencies of heterocyclic aromatic compounds has appeared in the literature and even the spectra of polycyclic aromatic hydrocarbons have not been dealt with at all extensively. BELLAMY,⁽¹⁰⁾ and JONES and SANDORFY⁽¹¹⁾ however, indicate that many of the generalizations based on studies of benzene derivatives may be carried over quite successfully to polycyclic molecules and that the introduction of a heteroatom into a ring usually results in only minor changes in the characteristic skeletal frequencies of the corresponding hydrocarbon. In its effect on the frequencies associated with the hydrogen atoms attached to the ring, the heteroatom behaves as a substituted carbon atom.

In the spectra of the phenanthroline complexes between 600 and 2000 cm^{-1} , strong bands were observed in three frequency regions, namely between 700 and 900 cm^{-1} , between 1125 and 1250 cm^{-1} , and between 1400 and 1650 cm^{-1} . Nujol bands prevented observation of bands in the neighbourhood of 1380 and 1465 cm^{-1} while a very intense band due to the perchlorate anion obliterated frequencies due to the ligand in a region about 70 cm^{-1} wide centered around 1085 cm^{-1} . Strong bands in the 700–900 cm^{-1} region in spectra of aromatic hydrocarbons have been identified with motions of ring hydrogen atoms moving in phase out of the plane of the ring. The particular frequency at which such bands appear further has been shown to depend on the number of adjacent hydrogen atoms around the ring and has been used to determine substitution patterns. In phenanthroline, and also its complexes, two strong bands appeared at approximately 725 and 850 cm^{-1} . This is the number expected since there is one group of two and two groups of three adjacent hydrogen atoms in the ring system. In hydrocarbons, the frequency shifts upwards as the number of adjacent atoms in a group decreases. On this basis, the 725 cm^{-1} band is assigned to the out of plane motion of the hydrogen atoms on the heterocyclic rings and the 850 cm^{-1} band to the hydrogens on the centre ring. The multiple splittings which these bands exhibited in most of the spectra probably arise from out-of-plane hydrogen motions other than the one in which all atoms move in phase, and also possibly from overtones of low lying fundamentals in resonance. In the bipyridyl spectra, only one strong band was observed in this region as expected for two identical groups of four hydrogen atoms each. The pattern of splitting of all these bands appeared quite sensitive to small differences in the nature of the co-ordinated atom since this region of the spectrum was most characteristic of any given complex. The variations did not appear systematic however.

Not much can be said about the bands in the 1125–1250 cm^{-1} region except that

⁽¹⁰⁾ L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. John Wiley, New York (1954).

⁽¹¹⁾ R. N. JONES and C. SANDORFY, *Chemical Applications of Spectroscopy*, Vol. IX, *Technique of Organic Chemistry* Chap. V. Interscience Publishers, New York (1956).

they may arise from in-plane hydrogen deformation motions or possibly ring vibrations. Even in the case of many simple aromatic compounds, satisfactory assignments for bands in this part of the spectrum are not available. The observed positions of the bands in the complexes varied somewhat from metal to metal but the shifts were scarcely large enough to justify any attempts at correlations.

It is in the third region that characteristic ring frequencies of aromatic compounds occur, both in monocyclic and polycyclic compounds and in heterocyclic as well as

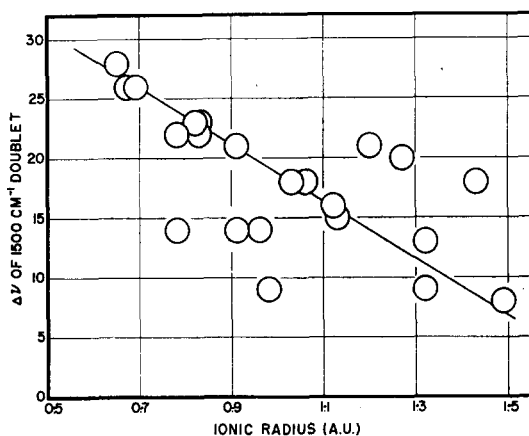


FIG. 4.—Separation between the two components of the 1500 cm^{-1} doublet vs. the ionic radius of the metal ion in 1:10-phenanthroline complexes.

carbocyclic. Perhaps the most typical and usually the most intense of these ring frequencies are one close to 1500 cm^{-1} and a second in the neighbourhood of 1600 cm^{-1} , the latter often consisting of more than one maximum. For example, in phenanthrene the first occurs⁽¹²⁾ at approximately 1500 cm^{-1} and the second at about 1605 cm^{-1} with a second component some 25 cm^{-1} or so higher. A third strong band occurs at about 1450 cm^{-1} . The spectrum of 1:10-phenanthroline is quite similar, the one band occurring at 1505 cm^{-1} , the second appearing as a triplet with the centre component at 1590 cm^{-1} and the third band shifting to 1423 cm^{-1} . Reference has been made previously to the fact that all these bands move to higher frequencies on coordination. The 1423 cm^{-1} band was least sensitive in this respect but the other two showed a clearly discernable shift of the order of 10 to 25 cm^{-1} . In addition, in all the complex spectra observed, the 1505 cm^{-1} band exhibited a weak satellite on its low frequency side. In some of the spectra, this component was present as a shoulder but in most it appeared as a sharp and well defined, though weak, band. The separation of the two maxima varied from metal to metal and several correlations with various properties of the metal ion were tried. It was found that the splitting varied in a direct manner with the ionic radius of the metal ion although the relationship was not as striking as one might wish since the magnitude of the separation did not exceed 30 cm^{-1} in any one case. The correlation is shown in Fig. 4. Similar, though not quite as good, correlations with the ionic radius were also noted for the mean position of the triplet at 1600 cm^{-1} , and for the separation between the 725 and 850 cm^{-1} bands.

⁽¹²⁾ C. G. CANNON and G. B. M. SUTHERLAND, *Spectrochim. Acta* **4**, 373 (1951).

These observations suggest that the size and consequent polarizing effect of the metal ion exercises a small but observable influence on the distribution of the electrons in the ring system. Co-ordination of the phenanthroline to a proton instead of to a metal ion resulted in a significantly greater splitting of the 1500 cm^{-1} band and also greater shifts of the other bands. Since the proton has a much smaller size and consequently a greater polarizing effect, the electrostatic picture is consistent.

The spectra of 2:2'-bipyridine and its complexes in general were less complicated than those of phenanthroline. Only three strong bands were present, one near 760 cm^{-1} ascribed to out of plane bending of ring hydrogens as mentioned previously, one near 1450 cm^{-1} which is probably a ring frequency, and a ring frequency near 1600 cm^{-1} . Numerous weak bands were observed between 900 and 1300 cm^{-1} . No close similarity to the phenanthroline spectra was noted except for the two ring frequencies. The absence of a strong band near 1500 cm^{-1} suggests that this particular ring frequency in the phenanthroline compounds is associated with the carbocyclic ring. No correlations with properties of the metal were apparent although the small number of complexes examined made attempts difficult.

EXPERIMENTAL

Spectroscopic. The infra-red absorption spectra were obtained with a Perkin-Elmer Model 21 spectrometer equipped with NaCl optics. All substances were examined as Nujol mulls. The frequencies tabulated for the various bands are considered to have an uncertainty of $\pm 5\text{ cm}^{-1}$ below 1800 cm^{-1} while the reproducibility generally was $\pm 1\text{ cm}^{-1}$ on the sharp bands and $\pm 2\text{ cm}^{-1}$ on most of the rest. Due to the presence of Nujol bands, the hydrogen stretching region yielded little information except to confirm the existence of a hydrate where it existed.

Analytical. All compounds were analysed for nitrogen and, wherever practicable, for metal content and carbon and hydrogen.* Since most of the compounds undergo violent decomposition on heating, melting points were not determined. The 1:10-phenanthroline monohydrate and 2:2'-bipyridine were obtained from the G. Frederick Smith Chemical Co. and used without further purification.

1:10-Phenanthroline. The anhydrous material was obtained on drying the monohydrate *in vacuo* at 110°C over phosphorous pentoxide.

1:10-Phenanthroline perchlorate. The salt was isolated as an amorphous precipitate after adding a slight excess of perchloric acid to an aqueous solution of the free base. Recrystallization from water converted the product into glistening white needles. (Found: C, 51.2; H, 3.15; N, 9.94. Calc. for Phen. HClO_4 : C, 51.4; H, 3.21; N, 9.97%.)

Lithium complex. Attempts to isolate a lithium complex of definite composition following the procedure reported by PFEIFFER and CHRISTELET⁽¹³⁾ for the preparation of mono-(1,10-phenanthroline)-lithium(I) perchlorate were unsuccessful. The products obtained most likely were mixtures of complexes since the spectra showed no significant absorption due to free ligand, its hydrate or its perchlorate salt. The following analysis was obtained for the material whose spectrum is presented. (Found: Li, 1.34; C, 60.7; H, 4.12; N, 10.4. Calc. for $\text{LiC}_{12}\text{H}_8\text{N}_2\text{ClO}_4$: Li, 2.41; C, 50.4; H, 2.79; N, 9.77. Calc. for $\text{Li}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{ClO}_4$: Li, 1.48; C, 61.7; H, 3.42; N, 12.0%.)

Bis-(1:10-phenanthroline)-sodium(I) perchlorate. Prepared according to the method of PFEIFFER and CHRISTELET⁽¹³⁾ who report the air dried substance to be the trihydrate. In the present work, the air dried product suffered no loss in weight on drying *in vacuo* over P_2O_5 at 110° . Found: C, 59.4; H, 3.24; N, 11.7. Calc. for $\text{Na}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{ClO}_4$: C, 59.7; H, 3.31, N, 11.6%.)

Tetra-(1:10-phenanthroline)-calcium(II) perchlorate trihydrate. A pure product could not be isolated according to the method in the literature.⁽¹³⁾ Since the infra-red spectrum closely resembled those of the other alkaline earth metals and showed no bands attributable to uncomplexed ligand, it has

* Carbon, hydrogen and nitrogen analyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

⁽¹³⁾ P. PFEIFFER and W. CHRISTELET, *Z. Anorg. Chem.* **239**, 133 (1938).

been included. The analysis suggests that the material is a mixture of the tris- and tetra-(1:10 phenanthroline) calcium(II) perchlorates. (Found: C, 52.4; H, 3.51; N, 11.9; Ca, 4.58; H₂O, 5.50. Calc. for Ca(C₁₂H₈N₂)₄(ClO₄)₂·3H₂O: C, 56.7; H, 3.74; N, 11.0; Ca, 3.95; H₂O, 5.32%).

Tetra-(1:10-phenanthroline)-strontium(II) perchlorate tetrahydrate. The method of PFEIFFER and CHRISTELEIT⁽¹³⁾ was followed. (Found: C, 53.2; H, 3.81; N, 10.2; Sr, 8.18; H₂O, 6.94. Calc. for Sr(C₁₂H₈N₂)₄(ClO₄)₂·4H₂O: C, 53.5; H, 3.71; N, 10.4; Sr, 8.11; H₂O, 6.67%).

Tetra-(1:10-phenanthroline)-barium(II) perchlorate tetrahydrate. The literature procedure⁽¹³⁾ was followed. (Found: C, 50.8; H, 3.44; N, 10.0; Ba, 12.11; H₂O, 6.33. Calc. for Ba(C₁₂H₈N₂)₄(ClO₄)₂·4H₂O: C, 51.1; H, 3.54; N, 9.92; Ba, 12.17; H₂O, 6.38%).

Tetra-(1:10-phenanthroline)-manganese(II) perchlorate dihydrate. A solution of 0.17 g of MnSO₄·H₂O and 0.60 g of the phenanthroline monohydrate in 100 ml of hot water was treated with 0.25 g of sodium perchlorate. Colourless needles were obtained after recrystallization of the precipitate from water. (Found: C, 57.9; H, 3.68; N, 11.1; Mn, 5.36; H₂O, 4.3. Calc. for Mn(C₁₂H₈N₂)₄(ClO₄)₂·2H₂O: C, 57.1; H, 3.56; N, 11.1; Mn, 5.43; H₂O, 3.6%).

Tris-(1:10-phenanthroline)-manganese(II) perchlorate. This compound was obtained as a pale yellow powder upon heating the tetra complex *in vacuo* at 185° over P₂O₅. (Found: C, 54.3; H, 3.24; H, 10.6; Mn, 6.81. Calc. for Mn(C₁₂H₈N₂)₃(ClO₄)₂: C, 54.4; H, 3.04; N, 10.6; Mn, 6.91%).

Tris-(1:10-phenanthroline)-iron(II) perchlorate. Prepared by adding 0.30 g of sodium perchlorate to a solution of 0.39 g Fe(NH₄)₂(SO₄)₂·6H₂O and 0.60 g of the phenanthroline monohydrate in 50 ml of hot water. Recrystallization of the amorphous product from hot water gave dark red crystals. (Found: C, 54.2; H, 3.10; N, 10.2. Calc. for Fe(C₁₂H₈N₂)₃(ClO₄)₂: C, 54.4; H, 3.02; N, 10.6%).

Tris-(1:10-phenanthroline)-iron(III) perchlorate monohydrate. Chlorine gas was introduced into a solution of 0.30 g of Fe(NH₄)₂(SO₄)₂·6H₂O, 0.60 g of phenanthroline monohydrate and 0.2 ml of concentrated H₂SO₄ in 100 ml of water until the colour changed from red to light blue. A moderate excess of 30% NaClO₄ solution was then added and the mixture cooled in an ice bath. The blue crystalline product was washed several times with small portions of cold water and dried *in vacuo* at room temperature over Dehydrite. If not protected from sunlight, the isolated product slowly turned red in colour. (Found: C, 45.8; H, 2.86; N, 9.18; H₂O, 2.10. Calc. for Fe(C₁₂H₈N₂)₃(ClO₄)₃·H₂O: C, 47.4; H, 2.85; N, 9.20; H₂O, 1.97%).

Tris-(1:10-phenanthroline)-cobalt(II) perchlorate. A solution of 0.24 g of CoCl₂·6H₂O in 20 ml of ethanol was heated to boiling, treated successively with 0.60 g of phenanthroline monohydrate, 0.30 g of NaClO₄ and 200 ml of boiling water and then stored immediately in an evacuated desiccator. After 24 hr, the yellow-brown crystalline product was isolated, washed with small portions of water, and dried *in vacuo* at room temperature. (Found: C, 53.1; H, 3.15; N, 10.5. Calc. for Co(C₁₂H₈N₂)₃(ClO₄)₂: C, 54.2; H, 3.04; N, 10.5%).

Tris-(1:10-phenanthroline)-cobalt(III) perchlorate dihydrate. A solution of 0.24 g of CoCl₂·6H₂O, 0.60 g phenanthroline monohydrate, 2 ml hydrogen peroxide (30 per cent) and 2 ml concentrated HCl in 50 ml distilled water was evaporated to approximately 5 ml. On treating the resulting syrupy mixture with 100 ml of water followed by 1 ml perchloric acid (72 per cent), a golden yellow precipitate formed. Recrystallized from 50 ml of water containing 1 ml 30% hydrogen peroxide. (Found: C, 46.5; H, 3.06; N, 9.03; H₂O, 4.06. Calc. for Co(C₁₂H₈N₂)₃(ClO₄)₂·2H₂O: C, 46.4; H, 3.00; N, 9.00; H₂O, 3.86%).

Tris-(1:10-phenanthroline)-nickel(II) perchlorate hemihydrate. Nickelous perchlorate was prepared *in situ* by treating 0.24 g of NiCO₃ with excess perchloric acid followed by evaporation to near dryness. After dissolving in 50 ml of water, the solution was treated with 1.2 g of phenanthroline monohydrate, heated for several minutes near boiling and then allowed to cool to room temperature. The resulting rose-red precipitate was recrystallized from water. (Found: C, 53.3; H, 3.18; N, 9.93; H₂O, 1.08. Calc. for Ni(C₁₂H₈N₂)₃(ClO₄)₂·½H₂O: C, 53.6; H, 3.10; N, 10.4; H₂O, 1.11%).

Bis-(1:10-phenanthroline)-copper(I) perchlorate. Prepared by adding a solution of 0.40 g phenanthroline monohydrate in 25 ml ethanol to a boiling solution containing 0.25 g CuSO₄·5H₂O, 0.2 g hydroxylamine hydrochloride, 1 ml conc. aqueous ammonia and 100 ml of water. While still boiling, the solution was treated with a slight excess of 10% NaClO₄ solution and the dark violet precipitate produced was further digested for 1 hr on the steam bath. The final product was washed well with water and dried at room temperature *in vacuo* over magnesium perchlorate. (Found: C, 55.3; H, 3.27; N, 10.7; Cu, 12.22. Calc. for Cu(C₁₂H₈N₂)₂ClO₄: C, 55.2; H, 3.08; N, 10.7; Cu, 12.14%).

Bis-(1:10-phenanthroline)-copper(II) perchlorate. Cupric perchlorate was prepared *in situ* by dissolving 0.08 g CuO in excess perchloric acid, evaporation to near dryness and dissolution in 100 ml distilled water. After heating to near boiling, 0.50 g phenanthroline monohydrate were added to this solution and the resulting amorphous blue-green precipitate was digested several hours on a steam bath. The crystalline product obtained was recrystallized from 80 ml of boiling methanol and dried *in vacuo* at room temperature. (Found: C, 46.2; H, 3.15; N, 9.11; Cu, 10.16. Calc. for $\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{ClO}_4)_2$: C, 46.2; H, 2.56; N, 9.00; Cu, 10.19%.)

Bis-(1:10-phenanthroline)-silver(I) perchlorate. Prepared by adding 0.13 g NaClO_4 to a solution of 0.17 g AgNO_3 and 0.60 g phenanthroline monohydrate dissolved in a mixture of 200 ml water and 200 ml methanol. The amorphous precipitate was digested 1 hr on a steam bath, filtered and recrystallized twice from nitrobenzene. The pale yellow crystalline product was dried *in vacuo* at room temperature. (Found: C, 51.2; H, 2.87; N, 9.93; Ag, 19.2. Calc. for $\text{Ag}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{ClO}_4$: C, 50.8; H, 2.82; N, 9.86; Ag, 19.0%.)

Tris-(1:10-phenanthroline)-zinc(II) perchlorate. A zinc perchlorate solution was prepared by dissolving 0.10 g zinc chloride in excess perchloric acid, evaporating nearly to dryness and redissolving in 200 ml distilled water. This solution was heated nearly to boiling, 0.60 g phenanthroline monohydrate were added and the mixture allowed to cool and stand overnight. The crystalline product obtained was washed with small portions of cold water, dissolved in a small amount of hot water and allowed to crystallize slowly. The final product was in the form of glistening needles with a slight tinge of pink suggesting a trace of iron contamination. (Found: C, 53.8; H, 3.08; N, 10.6. Calc. for $\text{Zn}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2$: C, 53.7; H, 2.98; N, 10.4%.)

Tris-(1:10-phenanthroline)-cadmium(II) perchlorate. A cadmium perchlorate solution was prepared by dissolving 0.12 g of the metal in a mixture of 1 ml conc. HNO_3 and 1 ml 72% HClO_4 , evaporating to dryness, and redissolving in 200 ml water. The complex was prepared in the same manner as the zinc complex. (Found: C, 50.7; H, 3.11; N, 9.70. Calc. for $\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2$: C, 50.7; H, 2.82; N, 9.85%.)

Tris-(1:10-phenanthroline)-mercury(II) perchlorate. This substance was obtained in the form of glistening white needles by following the procedure described for the zinc complex. (Found: Hg, 21.1; N, 8.76. Calc. for $\text{Hg}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2$: Hg, 21.3; N, 8.94%.)

Bis-(1:10-phenanthroline)-thallium(I) perchlorate. Prepared according to the procedure of PFEIFFER and WERDELMANN.⁽¹⁴⁾ (Found: C, 43.5; H, 2.41; N, 8.77; Tl, 30.0. Calc. for $\text{Tl}(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{ClO}_4$: C, 43.4; H, 2.41; N, 8.44; Tl, 30.6%.)

Tetra-(1:10-phenanthroline)-lead(II) perchlorate. Prepared by the method of PFEIFFER and CHRISTELEIT.⁽¹³⁾ (Found: Pb, 18.5; N, 10.3. Calc. for $\text{Pb}(\text{C}_{12}\text{H}_8\text{N}_2)_4(\text{ClO}_4)_2$: Pb, 18.4; N, 9.95%.)

Bis-(1:10-phenanthroline)-lead(II) perchlorate. Prepared by heating the tetra-lead complex *in vacuo* at 185°. The loss in weight corresponded to two moles of phenanthroline per mole of starting complex. (Found: Pb, 26.9; N, 7.10. Calc. for $\text{Pb}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{ClO}_4)_2$: Pb, 27.0; N, 7.30%.)

Tris-(1:10-phenanthroline)-bismuth(III) perchlorate. Prepared by the method of PFEIFFER and CHRISTELEIT.⁽¹³⁾ A colourless crystalline product was obtained after two recrystallizations from 1 per cent acetic acid. (Found: Bi, 19.3; N, 8.20. Calc. for $\text{Bi}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_3$: Bi, 19.9; N, 8.02%.)

Tris-(1:10-phenanthroline)-tin(II) perchlorate. Preparation of this compound was attempted by the method reported in the literature⁽¹⁴⁾ and various modifications. In all cases, the spectral results showed that no co-ordination to the metal had occurred and that the phenanthroline was present only as the perchlorate.

Tris-(2:2'-bipyridine)-iron(II) perchlorate, *tris-(2:2'-bipyridine)-iron(III) perchlorate trihydrate*, *tris-(2:2'-bipyridine)-cobalt(II) perchlorate*, *tris-(2:2'-bipyridine)-cobalt(III) perchlorate trihydrate* and *tris-(2:2'-bipyridine)-nickel(II) perchlorate*. These complexes were prepared according to the procedures given by BURSTALL and NYHOLM,⁽¹⁵⁾ and their compositions confirmed by analysis.

Tris-(2:2'-bipyridine)-manganese(II) perchlorate. Prepared by adding a solution of 0.62 g bipyridine in 5 ml methanol to a solution of 0.17 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 100 ml distilled water. The mixture was heated to effect solution, an excess of solid NaClO_4 added and the precipitate isolated after cooling to room temperature. Recrystallization from hot water yielded a bright yellow crystalline product. (Found: C, 50.1; H, 3.44; N, 11.7. Calc. for $\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2$: C, 49.9; H, 3.32; N, 11.6%.)

⁽¹⁴⁾ P. PFEIFFER and BR. WERDELMANN, *Z. Anorg. Chem.* **261**, 197 (1950).

⁽¹⁵⁾ F. H. BURSTALL and R. S. NYHOLM, *J. Chem. Soc.* 3570 (1952).