duced because of the improbably high atomic polarization value 14.4, which they gave.

Electron diffraction measurements[24] on perfluorocyclobutane have shown the four-membered ring to be non-planar, with a carbon–carbon distance of 1.60 Å., distinctly larger than the normal carbon–carbon distance, 1.54 Å. This structure seems to be determined by the repulsion between the fluorine atoms, since the distance of closest approach between fluorine atoms attached to adjacent carbon atoms is 2.73 Å., or twice the van der Waals radius of fluorine.[24] No moment was found for this compound, showing that its structure contains no net electrical dissymmetry, which is not inconsistent with the puckered ring structure proposed by Lemaire and Livingston.

From a purely geometrical point of view, the moment of pentafluoroethane should be the same as that of trifluoromethane, 1.62, since the resultant moment of three C–F dipoles making an angle of 110° with one another should be equal to that of one C–F dipole, and the moment of pentafluorochloroethane should be the same as that of trifluorochloromethane, 0.46. In view of the possible differences in the various factors determining the molecular moments, the observed values, 1.54 and 0.52, may be regarded as surprisingly close to the geometrically calculated values. In the analogous case of pentachloroethane and chloroform, the moment of the former, 0.92, is 0.10 lower than that of the latter, a difference indistinguishable from that between pentafluoroethane and trifluoromethane.

The moment of trifluorochloroethylene, 0.20, is slightly lower than those of CF_3Cl and C_2F_5Cl, which, to some extent, might be expected from the presumably smaller inductive lowering of the C–Cl moment by the C–F dipoles on the other carbon. However, the difference between the interactions of the chlorine and the fluorines with the double bond should also affect the moment.

The moment of dimethyl ether, 1.29, may be treated as the resultant, $2m \cos 111°$, of two moments, $m = 1.12$, acting in the directions of the C–O bonds. As an approximation, the molecule of perfluorodimethyl ether may be treated as containing two moments equal to that of trifluoromethane, 1.62, acting in opposite directions to the two moments, 1.12, and, therefore, giving a resultant moment, $2(1.62 - 1.12) \cos 111° = 0.58$, in good agreement with the observed value, 0.54. The moment of perfluorodiethyl ether is lower than that of perfluorodimethyl ether by almost the same amount, 0.13, as the difference between diethyl and dimethyl ethers.

It is evident that electrostatic inductive effects play an important part in determining the moments of the twelve molecules which have been discussed. The fact that they are sufficient to account in a semi-quantitative fashion for many of the observed moments and the differences between them does not, however, mean that the incalculable factors determining the bond moments are not altered somewhat by their environment. The net effect of these alterations on the moment would evidently be a change that is small or in the same direction as the effect of electrostatic induction.

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[24] H. P. Lemaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 (1952).

[CONTRIBUTION FROM THE DEPARTAMENTO DE FÍSICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO]

Studies on the Coördinate Bond. III. Absorption Spectra of Mono-α,α'-dipyridyl and Mono-o-phenanthroline Complexes[1]

BY KÔZÔ SONE,[2] P. KRUMHOLZ AND H. STAMMREICH

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The ultraviolet absorption spectra of mono-α,α'-dipyridyl and mono-o-phenanthroline complexes of cadmium, calcium, cobalt, copper, lead, magnesium, manganese, nickel, silver and zinc will be reported in this paper. The long wave length band of the mono-α,α'-dipyridyl complexes of the bivalent metal ions shows a characteristic splitting, the relative height of the two peaks depending on the stability of the complexes. A similar but less distinct splitting is observed in the short wave length band of the corresponding o-phenanthroline complexes. Approximate stability constants are reported for some of the complexes. The bathochromic shift of the absorption bands of the bases caused by complex formation is related to the difference between the stabilities of the complexes in the ground state and in their excited states.

The absorption spectra of complexes of metal ions generally show three more or less distinct groups of absorption bands.[3]

The first two groups may be attributed to the electronic excitation of (a) the metal atom (or ion) and (b) of the coördinated molecules (or ions), the energy levels involved being more or less perturbed by the formation of the complex. The last group may be attributed to electronic transitions involving those electrons, that participate directly in the coördinate bond.

It was thought that a detailed study of the absorption bands of the coördinated molecules could supply some useful information on the nature of the perturbation of their electonic levels due to the coördinate bond and possibly on the nature of the bond itself. α,α'-Dipyridyl and o-phenanthroline were selected as coördinated molecules, and the in-

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[1] Paper II, THIS JOURNAL, **75**, 2163 (1953).

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[3] See for instance, K. Yamasaki, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); R. Tsuchida, *ibid.*, **13**, 388, 436, 471 (1938); A. v. Kiss and D. V. Czegledy, *Z. anorg. Chem.*, **233**, 407 (1938); M. Linhardt and M. Weigel, *ibid.*, **266**, 49 (1951), and earlier papers; K. Sone, THIS JOURNAL, **75**, 5207 (1953). See also R. S. Mulliken, *ibid.*, **74**, 811 (1952).

fluence of the ions of bivalent cadmium, calcium, cobalt, copper, magnesium, manganese, nickel, zinc and lead and of monovalent lithium and silver on their ultraviolet absorption spectra[4] was studied. Conditions have been chosen, such that essentially only the 1:1 complexes were present in the solutions.

Experimental

Materials.—α,α′-Dipyridyl and *o*-phenanthroline were recrystallized from diluted ethanol to a constant melting point. Metal perchlorates were used throughout to minimize the formation of ion pairs. They were prepared by dissolving metallic oxides or carbonates of analytical purity in boiling perchloric acid (about 3 *M*) using a slight excess of the former. Such solutions contain a slight amount (a few tenths of a per cent.) of basic salt, except in the case of lead, where the amount of the latter is considerable. Such solutions were brought under potentiometric control nearly to the equivalence point by addition of perchloric acid. The solutions of the weaker complex forming metals, manganese, lead and silver were tested polarographically for the presence of stronger complex-forming ions, especially copper and zinc. They were found to contain less than 0.01%. The cobalt salt used contained about 0.3% nickel. As the absorption spectra of solutions containing only a moderate excess of cobalt (25 times over the concentration of the organic base) were practically identical with these measured in solutions containing a much larger excess these spectra cannot be seriously in error. The solutions of the perchlorates of magnesium, calcium and lithium were freed by means of sulfide ions from traces of heavy metals. The concentration of the latter was shown polarographically to be smaller than 0.001%.[5]

The solutions of the complexes were prepared by mixing aqueous solutions of the bases with variable amounts of the metal perchlorates. The concentrations of the bases in the final solutions were 4×10^{-5} for α,α′-dipyridyl and 1.5×10^{-5} *M* for *o*-phenanthroline. The concentration of the metal ions was varied between 10^{-3} and 5.10^{-1} *M*. Under such conditions the amount of other than the 1:1 complexes should be negligible. The *p*H of the solutions was near 5.5. It may be shown easily, using the known values of the proton affinities of α,α′-dipyridyl and *o*-phenanthroline,[6] that under our experimental conditions the formation of the corresponding NH ions will not seriously interfere with the complex equilibria, if the stability constants of the complexes are greater than about 10^3. This is the case except for the complexes of magnesium and calcium. In the latter cases (and for lithium) the *p*H of the solutions was maintained higher than *p*H 7. The presence of the small amount of basic metal salt in the solutions has no visible influence on the absorption spectra of the complexes, as shown by the independence of those spectra (of the stronger complexes) of the addition of small amounts of perchloric acid.

Measurements.—The ultraviolet absorption spectra were determined by using a Beckman D.U. spectrophotometer, equipped with thermospacers. Measurements were performed at an optical depth of 10 mm. and a temperature of 27 ± 1°. The reproducibility of the measured extinction values was about ±2%. In the case of the complexes of cadmium, cobalt, copper, nickel and zinc, variations of the absorption spectra were within the experimental error when the concentration of the metal ion was varied from 2×10^{-3} to 2×10^{-2} *M*. The spectrum of the silver complex of α,α′-dipyridyl indicated a slight dissociation of the complex at the lowest metal concentration employed. In the case of the complexes of lead, manganese and magnesium, the absorption spectra changed gradually with increasing concentration of the metal ion, indicating gradual formation of the complexes. In the case of the α,α′-dipyridyl complexes of lead and manganese, the absorption spectra showed no further changes if the metal ion concentration reached the value of about 10^{-1} *M*. The formation of the magnesium complex of α,α′-dipyridyl is only partial (see Fig. 2) even at a metal ion concentration of 5×10^{-1} *M*, whereas the corresponding complex of *o*-phenanthroline is only slightly dissociated under such conditions. Corresponding to the known stronger complexing power of *o*-phenanthroline the absorption spectra reveal the formation of a weak calcium complex of that base, whereas no such complex could be detected in the case of α,α′-dipyridyl. The spectra of both bases remain practically unchanged on the addition of lithium perchlorate in a concentration of 5×10^{-1} *M*.[7] An analysis of the absorption spectra of the weaker complexes at different metal ion concentrations permits an evaluation of the stability constants of the mono-α,α′-dipyridyl and mono-*o*-phenanthroline complexes. The given values may be taken only as rough approximations: Pb^{++} α,α′-Dip, $pK \simeq 3$; Mn^{++} α,α′-Dip, $pK \simeq 2.5$; Mg^{++} α,α′-Dip, $pK \simeq 0.5$; Mg^{++} *o*-Phen, $pK \simeq 1.5$; Ca^{++} *o*-Phen, $pK \simeq 0.5$.

Results

1. α,α′-Dipyridyl Complexes.—Our measurements on the mono-α,α′-dipyridyl complexes confirm (and extend) Yamasaki's[4] finding, that the ultraviolet absorption bands of α,α′-dipyridyl are shifted in its metal complexes to longer wave length, the long wave length (A) band being split in two more or less distinct peaks. Figure 1 shows as a typical example the absorption spectrum of the nickel mono-α,α′-dipyridyl complex together with the spectra of α,α′-dipyridyl and its NH ion. The spectra of all bivalent metals investigated in this study are similar to the spectrum of the nickel complex.[8] The spectrum of the magnesium complex could not be obtained fully, owing to the instability of the complex. Its gradual appearance with increasing metal concentration is shown in Fig. 2, indicating a qualitative similarity with the spectra of the other complexes. The absorption maxima of the complexes investigated are listed with the val-

Table I

Absorption Maxima (λ_{max}) and the Corresponding Molecular Extinction Coefficients (ϵ_{max}) of α,α′-Dipyridyl and its 1:1 Complexes

Complex-forming ion	$\lambda_{max.}$	$\epsilon_{max.} \times 10^{-3}$	$\lambda_{max.}$	$\epsilon_{max.} \times 10^{-3}$	$\lambda_{max.}$	$\epsilon_{max.} \times 10^{-3}$
. .	2800	13.3			2330	10.2
H	3010	15.5			2390	7.5
Ag	2900	12.8				
Cu	3000	15.5	3100	15.8		
Pb	3000	15.0	3100	13.5		
Ni	2945	16.7	3055	18.7	2440	11.2
Zn	2950	17.2	3060	17.7	2440	10.7
Co	2950	16.0	3040	16.0	2450	10.5
Cd	2950	17.2	3055	16.2	2440	10.2
Mn	2960	16.0	3060	14.5	2450	10.2
Mg	2940		3040			

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[4] Absorption spectra of several, mostly tris-α,α′-dipyridyl and *o*-phenanthroline complexes have been reported previously by K. Yamasaki and collaborators, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); **14**, 538 (1939); **15**, 130, 461 (1940); *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 137 (1948); *Proc. Japan Academy*, **29**, 337 (1953). The photographic technique employed generally in that work does not seem to be accurate enough for an analysis of the finer details of the spectra, in which we were mainly interested. At the high dilutions employed it is also probable that the weaker complexes were at least partly dissociated.

[5] The authors thank Dr. K. Bril for the performance of the polarographic analysis.

[6] See for instance P. Krumholz, This Journal, **73**, 3487 (1951).

[7] P. Pfeiffer and W. Christeleit, *Z. anorg. Chem.*, **239**, 133 (1938), prepared a complex between *o*-phenanthroline and lithium perchlorate in the solid state.

[8] In the case of copper, lead and silver the spectra of the complexes could be measured only for wave lengths greater than 2500 Å., owing to the strong absorption of the (hydrated) ions at shorter wave length.

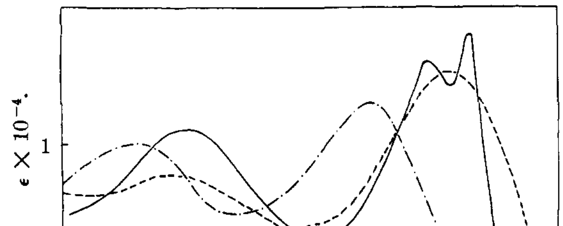

Fig. 1.—Ultraviolet absorption spectra of α,α'-dipyridyl (—·—·), α,α'-dipyridyl hydrochloride (------) and nickel mono-α,α'-dipyridyl perchlorate (——).

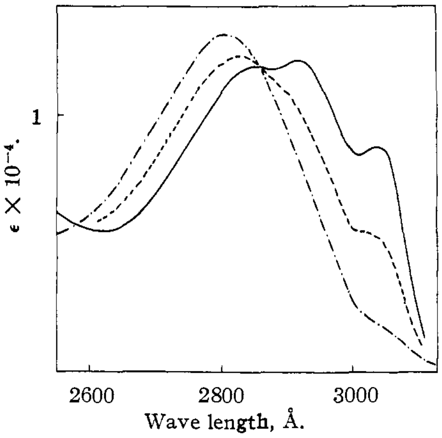

Fig. 2.—Influence of magnesium perchlorate on the absorption spectrum of α,α'-dipyridyl (4 × 10^{-5} *M*); (Mg^{++}) = 5 × 10^{-2} *M* (—·—·—), = 2.5 × 10^{-1} *M* (---), = 5 × 10^{-1} *M* (——).

ues of the corresponding molar extinction coefficients in Table I.

The position of the absorption maxima is nearly the same for the complexes of cadmium, cobalt, magnesium, manganese, nickel and zinc on the one hand and for copper and lead (only the A band was measured) on the other. In the case of other metal complexes, it was shown[9] that the bathochromic shift of the bands of the coördinated molecules increases with increasing stability of the complex. For the mono-α,α'-dipyridyl complexes investigated in this study no data of formation constants (except the approximate values given in the experimental part) are available. It may however safely be assumed that relative stabilities will follow in general the same order as found for most other complexes,[10] that is, Ni > Co, Zn > Cd > Mn and Cu > Pb. There is thus no visible direct relation between this order of stabilities and the extent of the bathochromic shift in the special case of the mono-α,α'-dipyridyl complexes. But as shown in Fig. 3, which represents the details of the particular splitting of the A band of several mono-α,α'-dipyridyl complexes, the relative height of the two absorption peaks follows, at least within the two groups mentioned above, exactly the expected order of stabilities. It may be interesting finally to note that the total oscillator strength[11] taken between the short wave minimum (λ ≃ 2200 Å.) and the long wave limit is the same within about 10% for α,α'-dipyridyl, its NH ion as well as for its complexes with cadmium, cobalt, manganese, nickel and zinc, even if the relative intensities of the single bands vary considerably.[12]

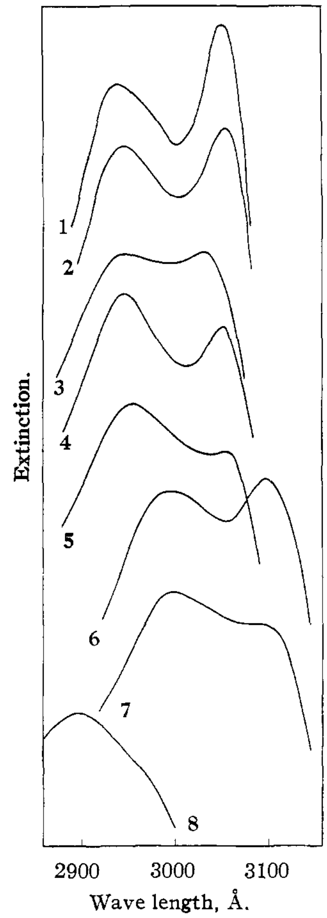

Fig. 3.—Absorption spectra of mono-α,α'-dipyridyl complexes of: 1, nickel; 2, zinc; 3, cobalt; 4, cadmium; 5, manganese; 6, copper; 7, lead; 8, silver. The spectra are drawn in the same scale but displaced vertically.

2. o-Phenanthroline Complexes.—The influence of metal and hydrogen ion bonding on the spectrum of o-phenanthroline is much less than in the case of α,α'-dipyridyl.[13]

The spectra of all metal complexes investigated are very similar, and the "individuality" of the spectra of the different complexes is still less pro-

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[9] K. Sone, I. Miyake, H. Kuroya and K. Yamasaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 70 (1948); K. Yamasaki and K. Sone, *Nature*, **166**, 998 (1950), and K. Sone, ref. (3).

[10] See D. P. Mellor and L. E. Maley, *Nature*, **159**, 370 (1947); H. Irving and R. J. P. Williams, *ibid.*, **162**, 746 (1948); *J. Chem. Soc.*, 3192 (1952); see also A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

[11] N. G. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

[12] A similar constancy of the total oscillator strength was shown (see ref. 6) to exist for all isomeric dipyridyls and phenylpyridines.

[13] We refrain from a reproduction of the spectra of the mono-o-phenanthroline complexes as those are essentially similar to the spectrum of the bis-o-phenanthroline–zinc complex given recently by J. M. Kruse and W. W. Brandt, *Anal. Chem.*, **24**, 1306 (1952); see also Yamasaki, ref. 4. For the spectra of o-phenanthroline and its NH ion see P. Krumholz, ref. 6.

nounced than in the case of α,α′-dipyridyl.[14] Table II summarizes the positions and intensities of the absorption maxima of the mono-*o*-phenanthroline complexes investigated, compared with the spectra of the free base and its NH ion.

TABLE II

ABSORPTION MAXIMA (λ_{max}) AND THE CORRESPONDING MOLECULAR EXTINCTION COEFFICIENTS (ϵ_{max}) OF *o*-PHENANTHROLINE AND ITS 1:1 COMPLEXES

Complex-forming ion	λmax.	εmax. × 10^{-3}	λmax.	εmax. × 10^{-3}	λmax.	εmax. × 10^{-3}
..	2900 infl.	9.0	2650	29.5	2260	42
H			2710	33	2190	36
Cu	2940	10.3	2720	34.5		
Ni	2920	11.0	2700	36.5	2280	36.5
Zn	2920	11.0	2700	35.5	2260	36.5
Co	2910	11.0	2695	34	2260	36
Cd	2920	11.0	2700	35.5	2260	36.5
Mn	2900	11.5	2680	36	2260	37
Mg	2890	12	2690	35	2270	39
Ca	2890		2690		2260	

The inflection appearing in the spectrum of *o*-phenanthroline at about 2900 Å. appears in all complexes as a distinct band. It seems that the small bathochromic shift of this band is slightly greater in the stronger complexes than in the weaker complexes of calcium, magnesium and manganese. The same seems to hold for the band at 2650 Å. The strong band at 2260 Å. shows no marked bathochromic shift in the complexes, but as demonstrated in Fig. 4, a similar, although less clear splitting like that observed for the A band of the α,α′-dipyridyl complexes.

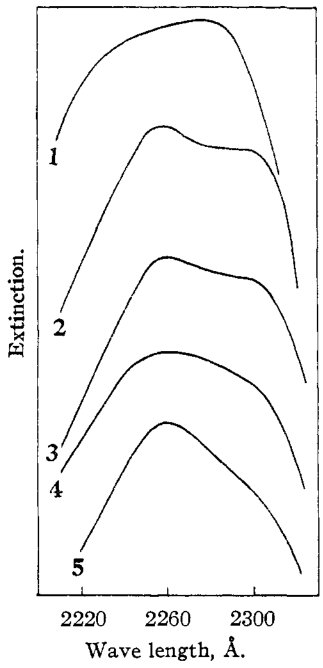

Fig. 4.—Absorption spectra of mono-*o*-phenanthroline complexes of: 1, nickel; 2, zinc; 3, cobalt; 4, cadmium; 5, manganese. The spectra are drawn in the same scale but displaced vertically.

Discussion

The experimental results show that no cogent relation exists between the stabilities of the mono-α,α′-dipyridyl and mono-*o*-phenanthroline complexes and the extent of the band shifts observed in their absorption spectra.[15] Such band shifts should be related to differences between the stabilities (or better heats of formation) of the complexes in the ground state and in their excited states, as recently proposed by Mulliken.[16]

The strong bathochromic shift of the absorption bands of α,α′-dipyridyl observed in its NH ion and metal complexes indicates that the excited state of this molecule has a greater tendency toward complex formation than its ground state (see ref. 16). The fact that complexes of widely different stabilities have almost identical absorption maxima shows that, in this special case, factors that increase the stability of the complex in the ground state (essentially a greater tendency of the metal ion toward covalent bonding[15]) are equally operative in the excited states.

The increased tendency of α,α′-dipyridyl toward complex formation in its excited states might be related to the increased polar character of such states (as compared with the ground state).[17] If this assumption is correct, it would mean an increase of the net negative charge on the nitrogen atoms, the most electronegative atoms of the molecule. This in turn should enhance the tendency of the α,α′-dipyridyl molecule to form complexes, because of an increase of the electrostatic interaction with the acceptor as well as because of an increase of the electron donating power of the nitrogen atoms.

The bathochromic shifts observed in the spectra of the *o*-phenanthroline complexes are much smaller than those found for the α,α′-dipyridyl complexes. This would mean that the electronic density on the nitrogen atoms is less affected by an electronic excitation in the former, than in the latter case.

The characteristic splitting of the A band of α,α′-dipyridyl in its complexes with bivalent metal ions may represent a vibrational structure. This supposition is supported by the fact that the distance between the two peaks is nearly the same (1100 ± 100 wave numbers) in all complexes investigated and has about the same absolute value as strong vibrational frequencies found in the Raman spectrum of α,α′ dipyridyl.[18]

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[14] Our measurements cover the range up to 3000 Å. and do not refer to absorption bands of low intensity, occurring at higher wave length, as reported by G. L. Roberts and F. H. Fields, THIS JOURNAL, **72**, 4232 (1950), and K. Yamasaki, ref. 4.

[15] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953), caution against any oversimplified treatment of absorption spectra of metal complexes as related to their stabilities.

[16] R. S. Mulliken, ref. 3, page 816. It may be easily shown by means of a thermodynamic cycle, that at least for 0,0 transitions and in absence of interactions with the solvent, the extent of a band shift produced by complex formation equals the difference between the heats of formation of the complex in the ground state and in the corresponding excited state.

[17] We restrain from writing down the somewhat doubtful resonance formulations for the excited, polar structures.

[18] To be published elsewhere.