

appears that Adamson, Welker and Wright have extrapolated the former workers results to changes in cold solutions on standing; however, the experimental conditions differ greatly in these two cases.

This investigation should be regarded as only a preliminary study on photodissociation in complex cyanide systems but it is of interest in that it gives further examples of slow dissociation in inorganic compounds.

As a preliminary empirical classification, it may be stated that those complex cyanides which are relatively unreactive toward acids, (*e.g.*, potassium hexacyanoferrate(II), potassium hexacyano-

ferrate(III), potassium hexacyanocobaltate(III) and potassium octacyanomolybdate(IV)), show a photodissociation effect, while those that are fairly easily decomposed by acids (*e.g.*, potassium hexacyanochromate(III) and potassium hexacyanomanganate(III)), show no such effect.

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Absorption Spectra of Some Metallic Chelate Compounds

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This paper points out that the absorption bands of about twenty chelate compounds of Co, Ni, Cu, Pd, Fe and other metals can be generally classified into (A) weak bands of the central metallic cations, and (B) strong bands due to the ligands. In some cases other band types appear. The formation of some of these anomalous bands may be due to the formation of a certain chromophore containing the metals, such as the band of covalent Ni chelates (Mellor, *et al.*) or some of the ferrous chelates indicated by the author. In some cases it is possible to indicate a connection between the extent of the shift of the ligand band caused by chelate formation and the stability of the chelate complex.

Introduction

Little is known about the absorption spectra of metallic chelate compounds. Smith, *et al.*,² report that a number of such compounds show intense visible bands differing considerably from their organic ligands, and central metallic cations. Mellor, *et al.*,³ found that the Ni chelates of square-planar dsp^2 covalent structure show a characteristic band near 400 $m\mu$ which is lacking in the Ni chelates of sp^3 ionic structure.

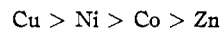
In earlier studies on the metallic complex salts of 2,2'-dipyridyl and 1,10-phenanthroline, K. Yamasaki and his collaborators⁴ reported that the visible and ultraviolet absorption spectra of the aqueous solutions were generally composed of: (A) weak absorption bands ($\log \epsilon$ 0-2) in the visible and near ultraviolet regions, characteristic of the central metallic cations, and similar to those bands observed in the hydrated and amine cations of the same metals; (B) very strong absorption bands ($\log \epsilon$ 4-5) in the ultraviolet region which were due to the organic ligand molecules and which were shifted somewhat toward longer wave lengths than the original positions found for the free ligand molecules.

They also reported that both bands were present in such chelates as those of Co(II), Co(III), Ni and

Cu, while in the case of Zn and Mn chelates only the latter (B) was observed. In the case of Fe(II) and Fe(III) chelates, a completely new type of absorption band, considerably stronger and quite different from those of Fe(II) and Fe(III) ions, appeared in the visible and near ultraviolet regions.

The author⁵ found that a number of other Fe(II) chelates also showed the same type of bands, and it was assumed that the formation of some sort of an unsaturated five-membered intramolecular ring containing ferrous ion acts as a chromophore to produce such absorption bands.

Studies on the absorption spectra of the metallic acetylacetonates carried out by the author and his collaborators,⁶ showed that the above-mentioned classification of absorption bands A and B was applicable, and that the Fe(III) chelate also showed a very anomalous absorption curve. Moreover, it was found that the shift of the band of acetylacetonate at 273 $m\mu$ produced by chelate formation was larger for the more stable trivalent chelates than for the divalent ones which are mainly of ionic character, and that for the divalent chelates, the magnitudes of these shifts were found to be in the order⁷:



(5) K. Sone, *Bull. Chem. Soc. Japan.*, **25**, 1 (1952).

(6) 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).

(1) Chemical Laboratory, Aichi College of Liberal Arts (Aichi-Gakugei-Daigaku), Higashiku, Nagoya, Japan.

(2) G. M. Smith, *et al.*, *THIS JOURNAL*, **62**, 1669 (1940); **63**, 3071 (1941); **64**, 1650 (1942); however, many of their observed bands might presumably be attributed to the deformed ligand bands discussed in this article.

(3) J. B. Willis and D. P. Mellor, *ibid.*, **64**, 181 (1942); **69**, 1237 (1947); H. A. MacKenzie, D. P. Mellor, J. E. Mills and L. N. Short, *J. Proc. Roy. Soc. New South Wales*, **78**, 70 (1944).

(4) K. Yamasaki, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); **14**, 538 (1939); **15**, 130, 461 (1940); K. Yamasaki, H. Yokoi and K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 137 (1948); *C. A.*, **44**, 9295 (1950).

(7) The ultraviolet spectra of the divalent chelates can be considered as the deformed ligand band, although in the Cu chelate a new band appears at *ca.* 245 $m\mu$. The Cu chelate does not obey Beer's law in the near ultraviolet region, and also shows a weak band at 640 $m\mu$ which is due to the Cu ion. Similar but weaker bands were observed also for Ni and Co(II) chelates. The ultraviolet spectra of trivalent chelates are very different from those of the divalent ones, and generally two bands appear at *ca.* 270 and 300-330 $m\mu$, both of which might be considered to be the ligand band extremely deformed from its original position. The visible and near-ultraviolet weak bands of Co(III) and Cr are those of the central cations; the band of the Fe(III) chelate in this region is quite anomalous as described in the text.

tered previously with other Fe(III) chelates (*cf.* Introduction). This seems to suggest the existence of some common origin for all such anomalous absorption bands shown by Fe(III) chelates and needs further study.

The former data of Moeller¹⁰ on Cu and Fe(III) chelates coincide approximately with that of the author, whereas those on Co(II) and Ni chelates are rather different. As far as the metallic chelates of the substituted 8-quinolinols are concerned, Phillips and Swank¹¹ measured the absorption curves of Fe(III) chelates of 8-quinolinol-5-sulfonic acid and 7-iodo-8-quinolinol-5-sulfonic acid, and found that anomalous absorption bands peculiar to Fe(III) chelates appeared at 445 and 580 $m\mu$ in the former compound and at *ca.* 610 $m\mu$ in the latter, respectively.

Absorption Spectra of Metallic Salicylaldehyde Chelates.—The absorption spectra of salicylaldehyde as measured by Morton and Stubbs, Daub and Vandenbelt, and Lemon,¹² have an absorption band at 325 $m\mu$ in neutral, and at 378 $m\mu$ in alkaline media. The absorption curves of the Cu, Ni and Co salicylaldehyde chelates between 265 and 450 $m\mu$ were quite similar in shape to that of the free ligand molecule in neutral media, with a strong band at 330–332 $m\mu$ ($\log \epsilon$ 3.75–3.9), whereas in the Cu and Ni chelates a large inflection was observed at *ca.* 400 $m\mu$ ($\log \epsilon$ *ca.* 2.5). No definite relation could be established between the shapes of these very similar curves and the stability series of Mellor and Maley. The origin of this similarity of absorption curves for various metal chelates can be explained by the assumption that the metal-ligand coordinate links in these chelates are relatively weak, and do not produce large differences for different metals. In fact, Calvin and Wilson¹³ and Mellor and Maley⁸ showed that the chelates of various metals with salicylaldehyde are more unstable than those of acetylaceton and 8-quinolinol.¹⁴

Absorption Spectra of Metallic Salicylaldoximates and Salicylaldiminates.—The absorption spectrum of salicylaldoxime in an alcoholic solution has two maxima at 305 and 265 $m\mu$, while Pd, Cu, Ni and Co chelates generally show two absorption bands at the longer wave lengths (Fig. 4). The curves for the Pd, Cu and Ni chelates are very similar, and in each case the position of the two maxima is shifted from the original position of the ligand bands to longer wave lengths in the following order:

	Ni	>	Pd	>	Cu
max.	305		275		270
	388		376		346 $m\mu$

If it is assumed that these bands are the deformed ligand bands as in the case of 8-quinolinol chelates, it can be expected that the stability of the chelates increases in this order from Cu to Ni. The higher

(11) J. P. Phillips, *THIS JOURNAL*, **72**, 3159 (1950); H. W. Swank and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 407 (1937).

(12) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940); H. W. Lemon, *THIS JOURNAL*, **69**, 2998 (1947); L. Daub and J. M. Vandenbelt, *ibid.*, **71**, 2416 (1949).

(13) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(14) It may be noted here that the Ni and Co chelates were dihydrates and that in the case of Cu chelate a weak band was observed at *ca.* 790 $m\mu$ ($\log \epsilon \approx 1$) which seems to be due to the Cu ion.

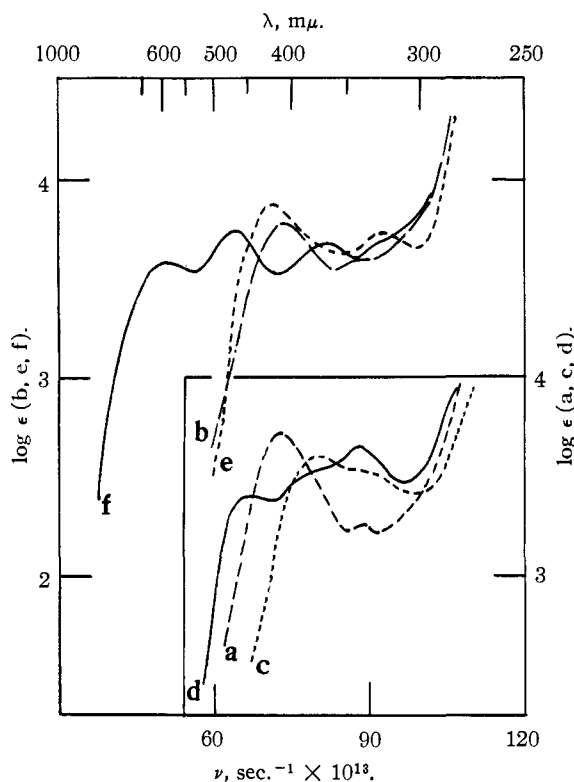


Fig. 3.—a, $\text{Cu}(\text{oxin})_2 \cdot 2\text{H}_2\text{O}$; b, $\text{Co}(\text{oxin})_2 \cdot 2\text{H}_2\text{O}$; c, $\text{Zn}(\text{oxin})_2 \cdot 2\text{H}_2\text{O}$; d, $\text{Ni}(\text{oxin})_2 \cdot 2\text{H}_2\text{O}$; e, $\text{Cr}(\text{oxin})_3$; f, $\text{Fe}(\text{oxin})_3$ all in chloroform (oxin = 8-quinolinol). The shapes of the spectra of $\text{Pd}(\text{oxin})_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Mn}(\text{oxin})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(\text{oxin})_2 \cdot 2\text{H}_2\text{O}$, and $\text{Co}(\text{oxin})_3$ are similar to those of the Cu, Co(II), Zn and Cr chelates, respectively. (a) The absorption curves of Pd, Cu, and Cr chelates in their alcoholic solutions were quite similar to those in chloroform solutions, excepting a shift of *ca.* 15 $m\mu$ of the principal maxima toward shorter wave lengths in the former case. (b) In addition to those bands shown in this figure, weak absorption bands ($\log \epsilon < 2$) were observed for some chelates in the visible region, although closer studies of these bands were made difficult by the generally slight solubilities of such chelates in chloroform or other organic solvents. These bands are probably due to the central metallic cations, and similar bands are often observed among other chelates (see later). Cell length, 1 cm.; Beckman DU quartz spectrophotometer; slit width, 0.04 mm. at 600 $m\mu$, 1.5 mm. at 300 $m\mu$; temp., 15–20°; concn., 1×10^{-4} to 6×10^{-5} mole.

stability of the Ni chelate, indicated in this way, seems to be of considerable interest with regards to the magnetochemical observation³ that this chelate possesses the square-planar dsp^2 covalent structure unlike the Ni chelates of acetylaceton, salicylaldehyde and 8-quinolinol, all of which have the sp^3 ionic structure. However, the band of the Ni chelate at 388 $m\mu$ can also be explained as the new type of absorption band which Mellor, *et al.*,³ have observed for a number of Ni chelates and considered to be characteristic of the Ni chelate with dsp^2 covalent structure, and it is also possible for this band to be the superposition of the two, *i.e.*, the deformed ligand band and this new band of Mellor, *et al.*, the view being supported by the somewhat split appearance of this band near the maximum position.

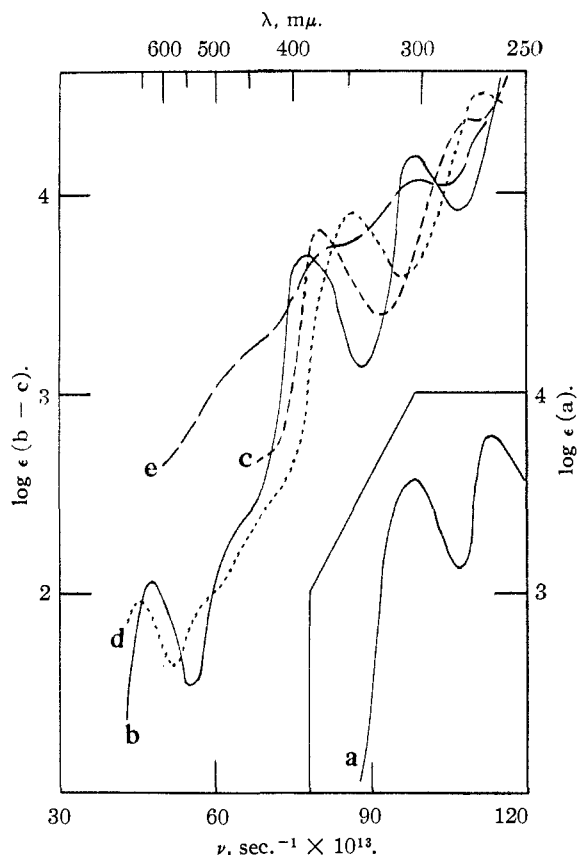


Fig. 4.—a, salicylaldoxime in alcohol; b, Ni-(salicylaldoxime)₂; c, Pd-(salicylaldoxime)₂; d, Cu-(salicylaldoxime)₂; e, Co(salicylaldoxime)₂. b-e in chloroform. Cell length, 1 cm.; Beckman DU quartz spectrophotometer; slit width, 0.04 mm. at 600 mμ, 1.5 mm. at 300 mμ; temp., 15–20°; concn., $1 \times 10^{-2} - 5 \times 10^{-5}$ mole.

The curve of the Co chelate is somewhat anomalous composed of a strong band at *ca.* 303 mμ and a large inflection at *ca.* 370 mμ. The strong continuous absorption of this chelate in the visible and near ultraviolet region is peculiar and may be attributed to the partial oxidation of the cobalt to trivalent state in solution, although the curve was fairly reproducible in repeated experiments.

The weak absorption bands of Cu and Ni chelates at 665 and 625 mμ, respectively, are due to the central metallic cations in each chelate.

The absorption curves of salicylaldimine chelates of Cu and Ni are similar to those of salicylaldoxime (Fig. 5), and here again the band of Ni chelate at *ca.* 410 mμ may be identified as that of covalent Ni chelates pointed out by Mellor, *et al.* The band shown by the Cu chelate at 570 mμ is due to the copper ion.¹⁵

Absorption Spectra of Metallic Dimethyl- and Diphenylglyoximates.—The absorption spectrum of neutral solution of dimethylglyoxime shows only a continuous absorption in the ultraviolet region, which shifts in alkaline solutions to longer wave lengths, forming a broad band at *ca.* 260 mμ.

(15) If it is assumed that the band at 320–340 mμ of the Ni chelate corresponds to that of the Cu chelate at 363 mμ, it follows that the stability relationship for these chelates would be Cu > Ni, *i.e.*, the reverse of that of the salicylaldoximates. It will be of interest to check these results with other methods.

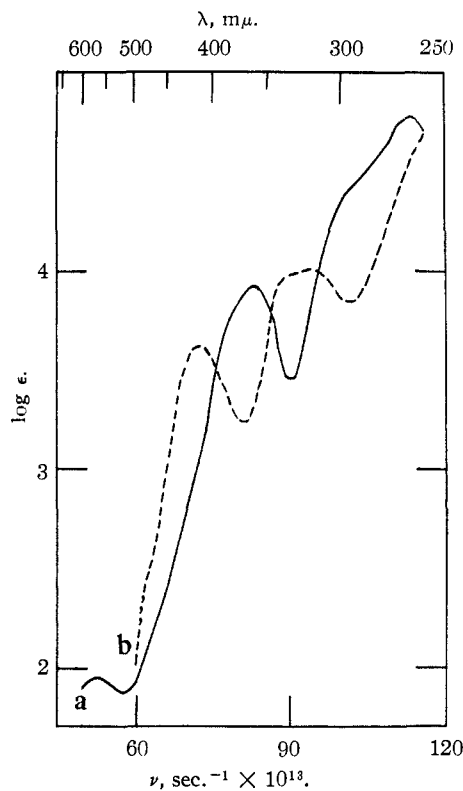


Fig. 5.—a, Cu-(salicylaldimine); b, Ni-(salicylaldimine); both in chloroform; cell length, 1 cm., Beckman DU quartz spectrophotometer; slit width, 0.04 mm. at 600 mμ, 1.5 mm. at 300 mμ; temp., 15–20°; concn., $1-1.6 \times 10^{-4}$ mole.

It was observed by Feigl¹⁶ that the Ni dimethylglyoximate, which is red in its solid state (and also in its colloidal solutions described by Juza¹⁷), showed yellow coloration when dissolved in chloroform or in some other solvents, thus presenting a striking color change with its state of dispersion. Thus, absorption measurements of this chelate were carried out: (A) in its chloroform solution (yellow), (B) in its colloidal solution (red) containing gelatin as the stabilizing agent, and (C) in its crystalline state (red), with the powder-reflection method.

The curve of the chloroform solution (Fig. 6) is very complicated; three new maxima appeared at 420, 375 and 328 mμ, among which the band at 375 mμ was the most pronounced and, judging from its position and intensity, this band probably belongs to the same category of bands mentioned by Mellor, *et al.*, for covalent Ni chelates.

The curves for the solid crystals and the colloidal solution are nearly identical and show distinct bands at *ca.* 550 and 405 mμ, the latter corresponds probably to the band at 375 mμ of the chloroform solution; but the band at 550 mμ is quite different in its shape, position and intensity from the bands of the chloroform solution, and it is highly probable that this new band is produced from some new electron transition which accompanies the closer interaction of the chelate molecules in

(16) F. Feigl, "Chemistry of the Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949.

(17) R. Juza and R. Langheim, *Angew. Chem.*, **50**, 255 (1937).

the crystal lattice or particles composing the colloidal solution.¹⁸

The Pd dimethylglyoximate shows a broad band at 383 $m\mu$, and also a strong band at 276 $m\mu$ which is probably due to the ligand molecule. Since the position of the latter is shifted to longer wave lengths than that of the Ni chelate (situated probably at *ca.* 265 $m\mu$), it can be supposed that the stability of the Pd chelate is higher than that of the Ni chelate. In fact, it is known that the Pd chelate is more stable to dilute mineral acids than the Ni chelate.¹⁶

The spectrum of the Ni diphenylglyoximate in chloroform is similar to that of Ni dimethylglyoximate, showing distinct bands at 407, 358 and 275 $m\mu$. The positions of bands are shifted toward longer wave lengths, and their intensities are also increased, in contrast to the dimethylglyoximate. These facts indicate the increased mobility of electrons in this chelate as the result of the introduction of the π -electron systems of phenyl groups into the resonance system of the chelate molecule.

The absorption spectrum of Ni dimethylglyoximate in colloidal solution was measured earlier by Juza and Langheim,¹⁷ and the recent results of Ferguson and Banks¹⁹ on the spectra of the colloidal solutions of analogous dioximates are similar to those of the present author.

Experimental

Preparation of Materials.—The 8-quinolinol chelates of Fe(III), Pd, Cu, Ni, Co, Zn and Cd were prepared by the usual analytical procedures,²⁰ and dried at room temperature. The 8-quinolinol chelates of Co(III) and Cr were prepared according to Ablov,²¹ whereas the salicylaldehyde, salicylaldoxime and salicylaldimine chelates were made according to Tyson, Adams and Ephraim.²² The glyoximates were prepared by conventional analytical methods, and the colloidal solution of the Ni dimethylglyoximate by Juza's method. All the prepared chelates were dissolved in hot chloroform, cooled and subjected to spectral measurements as promptly as possible.

Spectral Measurements.—A Beckman DU spectrophotometer was used throughout the study of ultraviolet regions, excepting some earlier data made with the Spekker spectrophotometer. Some data in the visible region were obtained and the powder reflection spectrum of Ni dimethylglyoximate was obtained with a self-constructed spectrophotometer composed of a RCA-931A multiplier phototube and a wave length spectrometer, the accuracy of which was about $\pm 2 m\mu$ in wave length and $\pm 3\%$ in extinction scales. For measurements of powder reflection spectra, the powdered sample painted on a white paper was supported ob-

(18) The author formerly considered the apparent similarity between the absorption curve of this colloidal solution and that of the Fe(II) dimethylglyoxime chelates as being due to their analogous electronic systems.⁵ However, if the above-mentioned color difference of the Ni chelate is taken into account, this explanation seems somewhat dubious.

(19) R. C. Ferguson and C. V. Banks, *Anal. Chem.*, **23**, 448 (1951).

(20) R. Berg, "Die analytische Verwendung von *o*-Oxychinolin "Oxin" und seiner Derivate," Ferdinand Enke, Stuttgart, 1938.

(21) A. Ablov, *Bull. soc. chim. France*, **53**, 234 (1933).

(22) G. N. Tyson and S. C. Adams, *THIS JOURNAL*, **62**, 1228 (1940); F. Ephraim, *Ber.*, **64**, 1215 (1931).

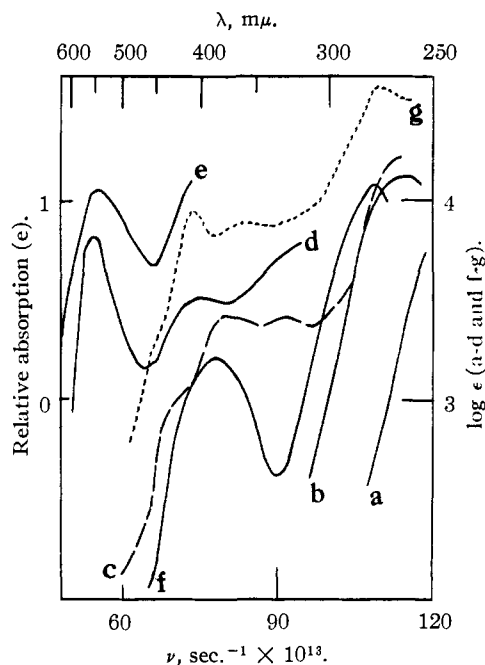


Fig. 6.—a-b, dimethylglyoxime, a in alcohol, b in 0.05 *M* KOH; c-e, Ni-(dimethylglyoxime), c in chloroform, d in aq. colloidal solution, e, powder reflection curve; f, Pd-(dimethylglyoxime); g, Ni-(diphenylglyoxime); f-g in chloroform. Relative absorption in the powder reflection curve was measured as $\log I_0/I_R$ where I_0 and I_R are the reflection intensities from white and painted surfaces. Cell length, 1 cm., Beckman DU quartz spectrophotometer; slit width, 0.04 mm. at 600 $m\mu$, 1.5 mm. at 300 $m\mu$; temp., 15–20°; concn., dimethylglyoxime and its complexes with Ni and Pd $2-3 \times 10^{-4}$ mole, diphenylglyoximate of Ni, 2.5×10^{-5} mole.

liquely in front of the spectrometer slit, and the reflected light from a 60-watt electric bulb was introduced into the spectrometer. The readings of the photocurrent were then compared with those of the white paper used as the blank test.

The absorption measurements at wave lengths shorter than *ca.* 260 $m\mu$ were made difficult by the strong absorption of chloroform.

The slight solubilities of many of the investigated chelates in chloroform made the preparations of sample solutions of accurate concentrations in many cases rather difficult, producing the probable error of *ca.* $\pm 10\%$ in the extinction readings. However, the shape and band positions of each curve were satisfactorily reproducible in most cases.

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