COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 26 ANNÉE 1980

Ultraviolet Spectra of Some Organic Compounds Containing Nitrogen and Their Complexes With Indium Trichloride

by

MARGUERİTE A. Wassef and MOHAMED GABER

14

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les diciplines scientifique représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III etait composé de trois séries

Série A: Mathématiques, Physique et Astronomie,
Série B: Chimie,
Série C: Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1: Mathématiques,
Série A_2: Physique,
Série A_3: Astronomie,
Série B: Chimie,
Série C_1: Géologie,
Série C_2: Botanique,
Série C_3: Zoologie.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Université d'Ankara. Elle accepte cependant, dans la mesure de la place disponible les communications des auteurs étrangers. Les langues Allemande, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagnés d'un resume.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, les dessins et figures portes sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extrait· sans couverture.

l'Adresse : Dergi Yayın Sekreteri,
Ankara Üniversitesi,
Fen Fakültesi,
Beşevler-Ankara

Ultraviolet Spectra of Some Organic Compounds Containing Nitrogen and Their Complexes With Indium Trichloride

By

MARGUERITE A. Wassef and MOHAMED GABER

Department of Chemistry, University College for Women, Ain Shams University, Cairo, Egypt.

(Received, 31 March, 1980 and accepted 18 July, 1980)

ABSTRACT

The ultraviolet spectral studies of the complexes formed between indium trichloride and nitrogen donors which contain more than one nitrogen atom as their potential sites of donation are considered. These studies reveal that the nitrogen atoms are incis-cis form in their indium trichloride complexes.

EXPERİMENTAL

Ultraviolet spectra were recorded on a VEB Carl Zeiss Jena Specord UV and VIS spectrophotometer. The spectra of the solutions were measured using silica cells 2-5 cm^3. The cells were cleaned by concn. HNO_3 acid then washed with small amounts of distilled water, followed by the solvent used and then by the solution.

Starting Materials.- (a) Hydrated indium trichloride (B.D.H); (b) 2,2′-bipyridyl (Riedel), m.p. 69°C; (c) 4,4′-dimenthyl 2,2′-bipyridyl (Riedel), m.p. 169°C; (d) o-phenanthroline (B.D.H.), m.p. 98-100°C[1]; (e) 2,9-dimethyl-ophenanthroline (B.D.H), m.p. 159°C and (f) 2,2′,2″-tripyridyl (Sigma grade), m.p. 169°C[1], were all reagent grades and were used without any further purification.

Compounds.- Reactions of stoicheiometric quantities of the above mentioned organic chelating ligands with indium trichloride were carried out in non-aqueous solvents. The compounds obtained were recrystallised from the appropriate solvents. Detailed study on these adducts are given elsewhere.[2]

Considerable care was taken with the drying of solvents. Ethanol was boiled under reflux with magnesium ethoxide and then distilled. Other solvents were dried by conventional methods.[3] Double distilled water was used.

Weighing of the compounds were carried out using a semimicro electric balance reading to the fourth decimal.

Melting points were measured using an ordinary Gallen kamp tube melting apparatus.

Analytical data for C, H and N were determined in the microanalytical unit. El-Nasr Company. Chloride[4] and indium[5] analyses were carried out in this lab.

Discussion

The absorption spectra of complexes of metal ions generally show three more or less distinct groups of absorption bands.[6]

The first two groups may be attributed to the electronic of (a) the metal atom (or ion) and (b) of the coordinated 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 coordinate bond.

It was thought that a detailed study of the absorption bands of the coordinated molecules could supply some useful information on the nature of the perturbation of their electronic levels due to the coordinate bond and possibly on the nature of the influence of the ions.

The ultraviolet spectra of 2,2′-bipyridyl at pH values ranging between 1.8 and 12 are reported.[7] In basic solution, two bands appear at 281 and 233 nm. It is clear from Fig. 1 and the values reported in Table 1, that the spectrum in basic solution is similar to those in organic solvents. Since the molecule is proved to be trans in organic solvents[8], these two bands can be attiributed to the characteristic absorption of the trans form. As shown in Fig. 2, the absorptions of 2,2′-bipyridyl adduct, $InCl_3$, 2 (bipy) at 281 and 237 nm obey Beey's law. Values for the variation of the optical densities with concentration are given in Table 2.

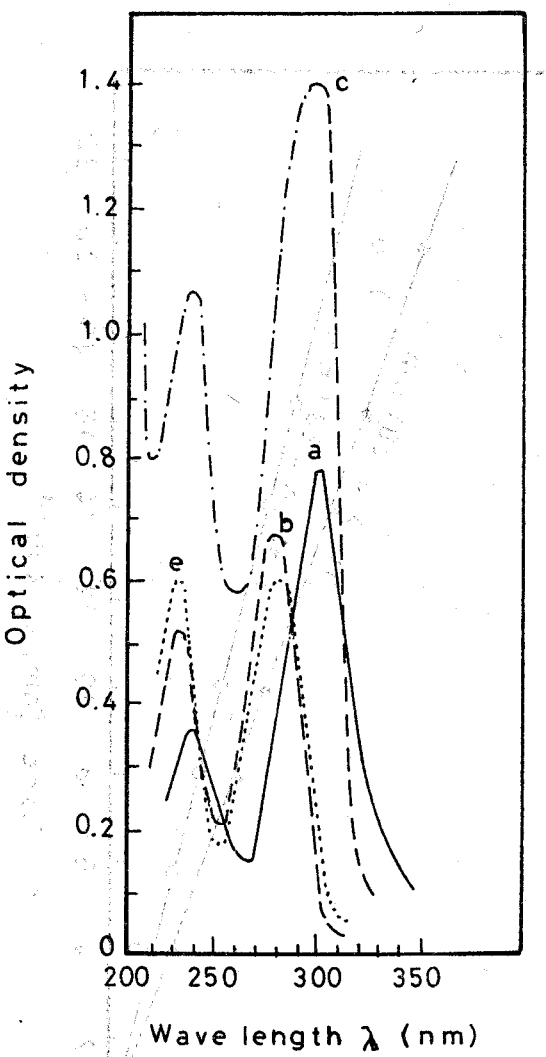

Fig. (1) Comparison of the spectra of 2,2′-bipyridyl.
——— (a) acidic solution (5×10^{-5} mole/ℓ),
– – – (b) basic solution (5×10^{-5} mole/ℓ),
..... (e) ethanolic solution (6×10^{-5} mole/ℓ and
—·— (c) complex (7.6×10^{-5} mole/ℓ)

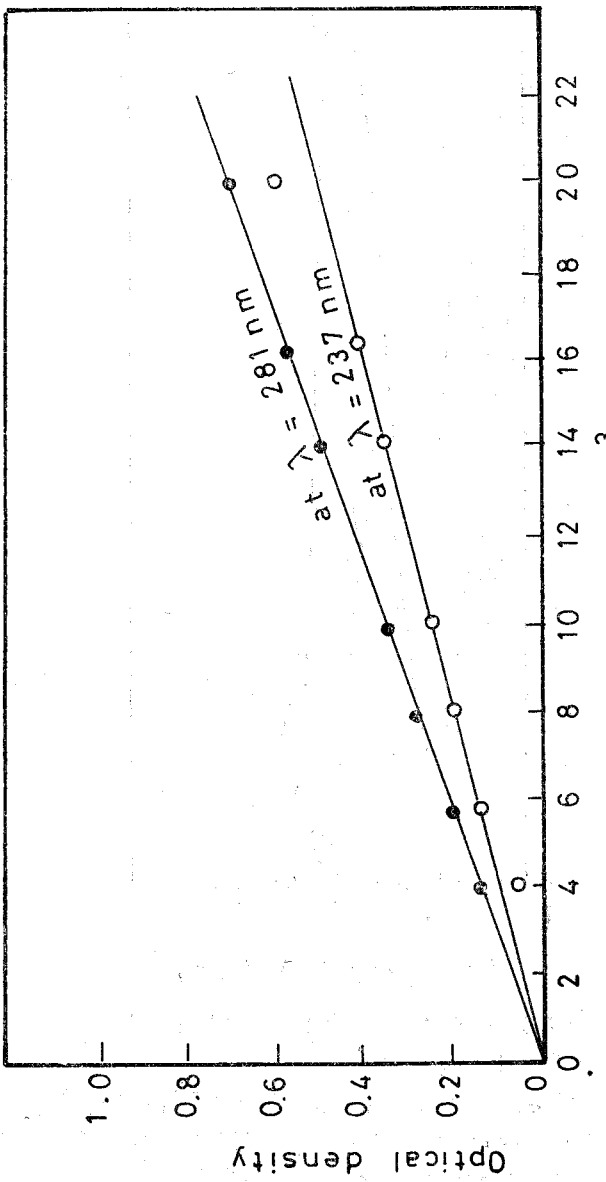

Fig. (2) The relation between the optical density and concentration for In Cl_3, 2(2,2′-biby), $2H_2O$.

Table 1

The Ultraviolet Spectra of 2,2′-bipyridyl and Indium Chloride Complexes in Various Solvents (nm)

Compound	Solvent	Protonated or chelated cis	trans	π_2
2,2′-bipyridyl	cyclohexane	———	283 (15.0)[a]	245 (11.3)[a] 237 (12.1)[a]
	chloroform	———	284 (14.5)[a]	245 (9.9)[a] 240 (10. 3)[a]
	ethanol	———	281 (10)[a]	244 (9.1)[a] 237 (13.6)[a]
	water (pH=12)	———	281 (0.69)[a]	233 (0.53)[b]
	water (pH=1.8)	301 (0.78)[a]	———	239 (0.37)[b]
$InCl_3$, 1.5 (bipy), H_2O	water	301 (18. 2)[b]	———	238 (13. 8)[a]
$InCl_3$, 2 (bipy), $2H_2O$	ethonol	———	281 (24. 6)[a]	244 (18. 2)[a] 237 (23. 2)[a]

f) The number denotes the molecular extinction coefficient (X 10^3).

b) The number indicates the absorbancy of 5 x 10^{-5} mole/L. solution in which two species are in equilibrium.

Table (= 2)

The Variation of Opetical Density with Concentration For $InCl_3$, 2 (bipy), $2H_2O$

Concn. gm/L X 10^{-3}	Optical Density λ 281 (nm)	λ 237 (nm)
20	0.70	0.60
16	0.69	0.65
14	0.49	0.35
10	0.34	0.24
8	0.29	0.20
5.7	0.20	0.14
4	0.12	0.06

The spectrum of 2,2′-bipyridyl in acidic solution exhibits two bands at 301 and 239 nm. It was shown by Krumholz[9] and Westheimer and Benfey[10] that the mono-cation predominates in ordinary acidic medium. Nakamoto[7] reported that the cis-form is expected to be more stable in acidic medium than the trans one. As shown in Fig. 1, the spectrum of 2,2′-bipyridyl in acidic medium is similar to that of its adduct indium trichloride. Similar results are reported for other bipyridyl complexes.[11]

The spectrum of the indium complex solution investigated in this study is similar to the spectrum of the silver complex[11] in which no splitting of the absorption bands are observed.

Fig. 3 shows the ultraviolet spectra of 4,4′-dimenthyl 2,2′-bipyridyl in water, acidic medium and in alcoholic solution, together with its indium trichloride complexes. As shown in this figure, the spectrum in acidic solution is similar to that of the indium complex. Values for λ_{max}nm of the 4,4′-dimethyl-2,2′-bipyridyl and its indium complex are given in Table 3.

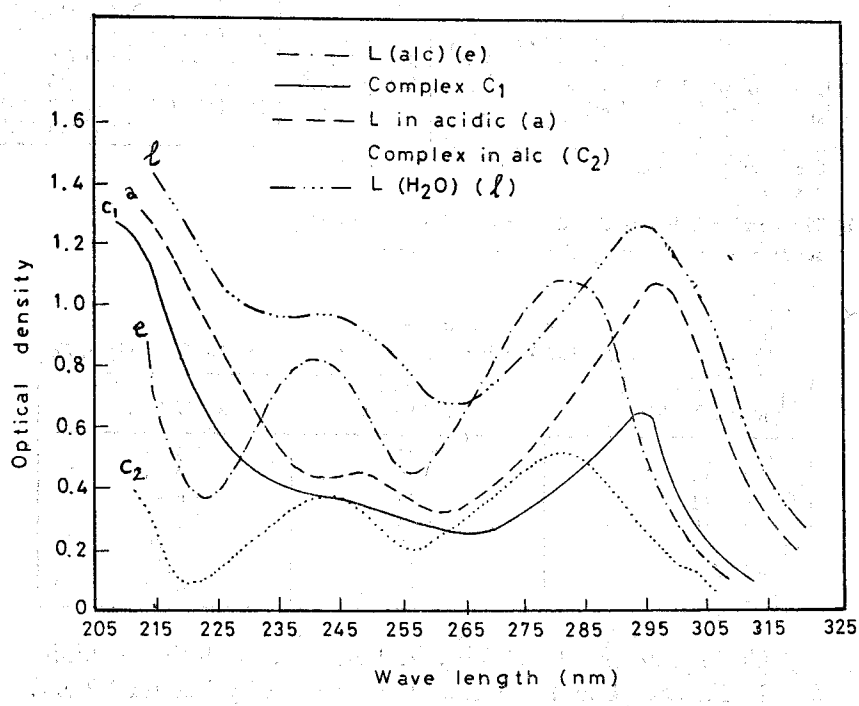

Fig. (3) Absorption spectra of 4,4′ dimethyl - 2,2′ - bipyridy (L) and its Indium chloride complex.

Following the same arguments as in the case of the bipyriyl complex, dimethyl bipyridyl molecule is in the cis-cis form in its indium complex.

Fig. 4 shows the ultraviolet spectra of 2,2′,2″-tripyridyl at various pH values in buffer solutions. Values for λ_{max}(nm) of tripyridyl together with its indium trichloride complex are given

Tablo 3.

Tbe Ultraviolet Spectra of 4,4′-dimethyl-2,2′-bipyridyl and Indium trichloride complexes in Various Solvants

Compound	Solvent	Protonated or chelated cis	Trans	π_1
4,4′-dimethyl-2,2′-bipyridy (L)	Cyclohexane	———	281	249 240
	Chloroform	———	281	244
	Ethanol	———	282 (10.8)[a]	241 (8.2)[a]
	Water (1.8)	298.5 (11.6)[a]	———	245 (5.1)[a]
$InCl_3$, 1.5L	Ethanol	———	303 (11.3)[a] v.wb 282 (13.3)[a]	243 (10.2)[a]
$InCl_3$, 1.5L	Water	298.5 (66)[a]	———	245 (38)[a]

f) The number denotes the molecular extinction coefficient (X 10^{-3}).
b) Indicates a shoulder.

in Table 4. As shown in Fig. 5, the spectrum of basic solution is similar to those in organic solvents in which the compound has two absorption maxima at 285 and 235 nm. Therefore, it is reasonable to conclude that the organic molecule is trans-trans form.

From a detailed study of the spectrum of 2,2′,2′′-tripyridyl, Nakamota[7] concluded that the most probable structure for a dicaiton is the cis-cis form.

As seen in Fig. 5 (aγb), the spectra of acidic solution and that of its indium complex exhibit three main bands at *ca.* 325, 285 and 231 nm, although the fine structures in the latter are blurred in the former. Blurring of these bands depends on the kind of the metal.[7]

The interval between 325 and 285 nm bands is too large to assign them to the vibrational structures belonging to the same electronic transition. Nakamoto[7] measured the ultraviolet spectra of metal chelate compounds of 2,2′,2′′-tripyridyl with various metals and reported that all these compounds exhibit three bands around 340-320, 285-270 and 235-220 nm.

The influence of metal and hydrogen ion bonding on the spectra of o-phenanthroline and its dimethyl compound (DM-o-phen.), Fig. 6, is much less than in the case of 2,2′-bipyridyl[6,12,13]. Table 5 summarises the positions and intensities of the complex of o-phenanthroline with indium trichloride, compared with the spectra of the free base and its NH ion.[14] Similar results for complexes of bivalent metal ions with o-phenanthroline are reported.[11]

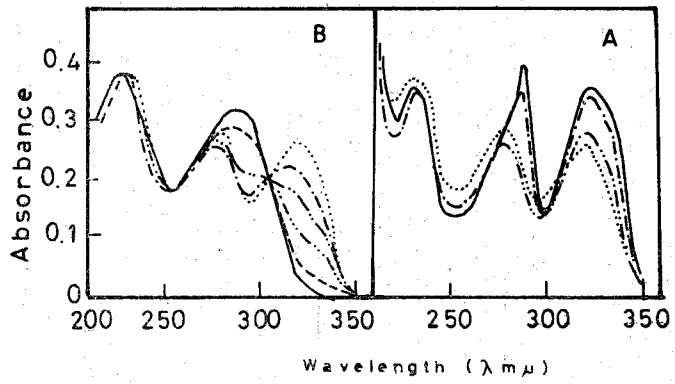

Fig. (4) Absorption Spectra of 2,2',2"-tripyridyl in Buffer solutions ($2x10^{-5}$ mole/L): A, in acidic solutions: -,pH 1.0; -.-., 3.0; -..-..,3.65; ....4.05.

B, in neutral and basic solutions, ...,4.05; -.-.,4.4;-..-.. 4.87; -...-..., 5.25; - - - , 5.83; ——, 12.0.

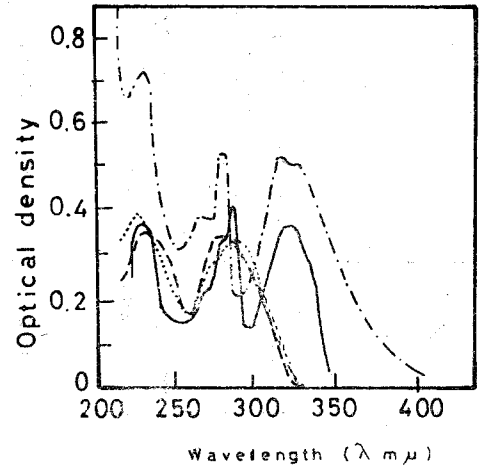

Fig. (5) Comparison of the Spectra of 2,2',2"-tripyridyl: -.-acidic solution ($2X10^{-5}$ mole/L):....(b)basic solution ($2X10^{-2}$ mole/L)——(e)ethanolic solution (10^{-5} mole/L)——,$InCl_3$,2,2',2"-tripy in H_2O (4.4×10^{-5} mole/L).

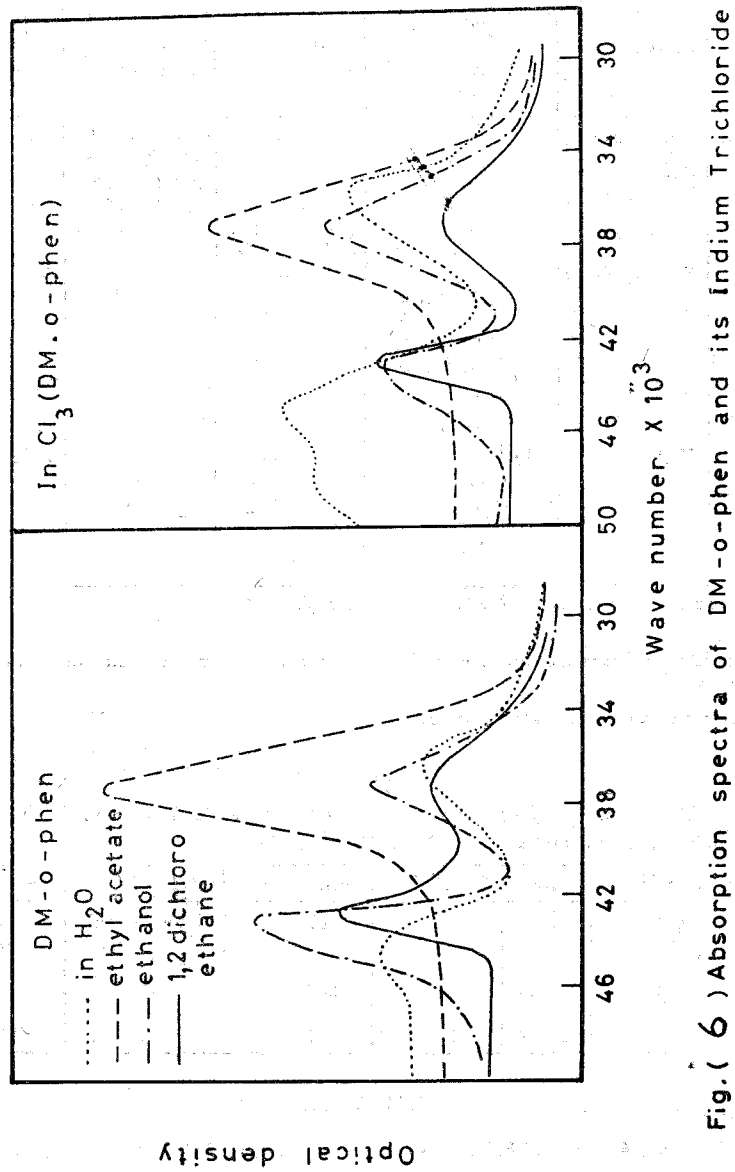

Fig. (6) Absorption spectra of DM-o-phen and its Indium Trichloride complex.

Table (4)

The Ultraviolet Spectra of 2,2′,2″-Tripyridyl in Various Solvents (nm) and its complex in water

Compound	Solvent	Protonated or chelated cis-cis	Protonated cis-trans	Trans-Trans	π_2
2,2′,2″-tripy (L)	Cyclohexane	———	———	278 (18. 8)[a]	235 (20. 4)[a]
	chloroform	———	———	280 (17. 9)[a]	240 (17. 2)[a]
	Ethanol	———	———	279 (18. 6)[a]	234 (19. 4)[a]
	Water(pH=12	———	———	290 (0.32)[b]	227 (0.39)[b]
	Water (pH_4)	———	(A) 320(0.28)[b]	———	232 (0.38)[b]
			(B) 279(0.29)[b]		
	Water(pH1.8)	(A) 333(0.3)[b] 322(0.36)[b]	———	———	231 (0.36)[b]
		(B) 288(0.41)[b] 280(0.33)[b] 270(0.22)[b]			
$InCl_3$,L	Water	(A) 333(19.7)[a]** 328(21.2)[a]** 286(21.5)[a]** 276(17.4)[a]** 267(14.0)[a]	———	———	232.5(28.8)[a]

d) The number denotes the molecular extinction coefficient ($X10^3$).

b) The number indicates tbe absorbancy of $2 X 10^{-5}$ mole/L. solution in which three species are in equilibrium

* Similar high values for ε are reported.[15]

Table (5)

Absorption Maxima (λ_{max}) (nm) and the corresponding Molecular Extinction Coefficient (ε_{max}) of o-phenanthroline and its Complex with Indium (III) Chloride

Compound	Solvent	λ_{max}	$\varepsilon_{max}X10^{-3}$	λ_{max}	$\varepsilon_{max}X10^{-3}$	λ_{max}	$\varepsilon_{max}X10^{-3}$
o-phen.	H_20	290	9	265	29.5	226	42
NHion	H_20			271	33	219	36
$InCl_3$,1.5 (o-phen)	H_20	292.4	7.4	267	26	227	31.5
$InCl_3$,2 (o-phen)$2H_20$	H_20	292.4	22.5	267	80	227	103

REFERENCES

1– Marguerite A. Wassef, Ph. D. Thesis, Univ. of London, 1967.

2– Marguerite A. Wassef and Mohamed Gaber, in preparation. send for publication in tbe Communications de La Faculte Des... D'Ankara 26 1980.

3- A.W Weissberger and E.S. Proskauer, "Organic Solvents, Physical Properties and Methods of Purification", Interscience, second edition, 1965.

4- A. Vogel, "Quantitative Inorganic Analytical Chemisty", Longman, London, Third edition, 1972.

5- A.J. Carty and D.G. Tuck, J. Chem. Soc. (1964) 6012. Sommer and Hnilickova, Naturwiss., (1958), 45, 544.

6- K. Yamasaki, Bull. Chem. Soc. Japan, 12, 300 (1937), R. Tsifchida, Ibid., 13, 388, 471 (1938).
A.V. Kiss and V. Canalady, Z. Anorg. Chem., 933, 407 (1938).

7- K. Nakamoto, J. Phys. Chem., 64, 1420 (1960).

8- P.E.Fielding and R.J.W. Lefevre, J.Chem. Soc., 1811 (1951).

9- D.E.C. Carbridge and E.G. Cox, J. Chem. Soc., 594 (1956).

10- F.H. Westheimer and O.T. Benfey, J. Am. Chem. Soc., 78, 5309 (1956).

11- K. Some, P.K. Krumbholz and H. Stammerich, J. Am. Chem. Soc., 77, 777 (1955).

12- J.M. Kruse and W.W. Brandt, *Anal. Chem.*, 24, 1306 (1952).

13- Yamasaki and Colloborators, Bull. Chem. Soc. Japan, 14, 538 (1939); Proc. Japan Academy, 29, 337 (1952).

14- P. Krumholz, J. Am. Chem. Soc., 73, 3487 (1951).

15- L. J. Andrews and R. M. Keefer, J. Amer. Chem. Soc., 73, 4169 (1951).

ÖZET

Azot ihtiva eden bazı Organik bileşiklerin U.V. Spektrumları ve indiyum triklorür ile oluşturdukları Kompleksler.

(2,2′-bipiridil ve onun 4,4′ -dimetil, e-fenantrolin, 2,9 -dimetil ve 2,2′ -2″ tripiridil türevleri) nin I.V. Spektrumları değişik ortamlarda incelenmiştir ve bileşiklerin, bazik organik ortamda trans-trans şeklinde, asidik ortamda ise cis - cis şeklinde olduğu isbatlanmıştır.

Bu çalışmalar sonunda, molekülünde iki veya daha fazla azot eden bu organik bileşiklerin triklorür komplekslerinin cis - cis şeklinde olduğu anlaşılmıştır.

Prix de l'abonnement annuel

Turquie: 15 TL; Etranger: 30 TL.
Prix de ce numèro: 5 TL (pour la vente en Turquie).
Prière de s'adresser pour l'abonnement à: Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi, Ankara – 1981