

Characterization Studies of Some Bi- and Tetradentate Bifunctional *Schiff* Base Complexes with Co(II), Ni(II), and Cu(II)

M. R. Mahmoud, S. A. Ibrahim*, and N. M. Ismail

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

(Received 21 November 1983. Revised 8 January 1984. Accepted 25 January 1984)

Co(II), Ni(II) and Cu(II) complexes of some bifunctional arylidene-*o*-phenylenediamine *Schiff* bases have been prepared. Formation, stoichiometry and stability of the complexes have been tested in solution using electronic spectral measurements. Characterization of the complexes has been accomplished primarily by elemental analysis, molar conductance as well as electronic and IR spectral measurements. It is concluded that the *o,o*-hydroxy derivative (L_1) acts as a bivalent ONNO tetradentate ligand while the molecules of the other derivatives (L_2 – L_5) are coordinated to the metal ions as bidentate NN ligands. The Cu(II)– L_1 complex is suggested to possess a tetrahedral geometry whereas the other complexes are suggested to exhibit a distorted octahedral geometry. The different bands observed in the electronic spectra of the complexes in *DMF* solutions have been assigned to the π – π^* , $L \rightarrow MCT$ and d-d electronic transitions.

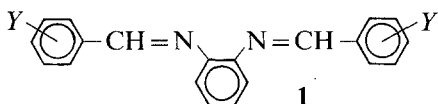
(Keywords: Complex formation constant; Conductance)

Untersuchungen zur Charakterisierung einiger zwei- und vierzähliger bifunktionaler Schiffbasen-Komplexe mit Co(II), Ni(II) und Cu(II)

Es wurden die Co(II)-, Ni(II)- und Cu(II)-Komplexe einiger bifunktionaler Aryliden-*o*-phenylenediamin-*Schiff*basen hergestellt. Unter Verwendung elektronenspektroskopischer Methoden wurde die Bildung, Stöchiometrie und Stabilität der Komplexe in Lösung untersucht. Die Charakterisierung erfolgte mittels Elementaranalysen, Leitfähigkeitsmessungen und Elektronen- bzw. IR-Spektroskopie. Es wird darauf geschlossen, daß das *o,o*-Hydroxyderivat L_1 als bivalenter vierzähliger ONNO Ligand wirkt, während die anderen Derivate (L_2 – L_5) als zweizählige NN Liganden an die Metallionen koordiniert sind. Für den Cu(II)– L_1 Komplex wird eine tetraedrische Geometrie vorgeschlagen, währenddessen die anderen Komplexe eine verzerrte octaedrische Geometrie aufweisen. Die in den Elektronenspektren der Komplexe in *DMF*-Lösung auftretenden Banden werden den π – π^* , $L \rightarrow MCT$ und d-d Elektronenübergängen zugeordnet.

Introduction

Continuing our studies on metal complexes of mono-, bi- and tridentate monobasic *Schiff* bases¹⁻⁵, we report here a study concerning the complexes of some bi- and tetradentate dibasic *Schiff* bases with the transition metal ions Co(II), Ni(II) and Cu(II). The study involves synthesis and characterization as well as the investigation of the effects of molecular structure of the *Schiff* base on the stability of the complex. The dibasic *Schiff* bases used are:



$Y = o\text{-OH}$, L_1 ; $=p\text{-H}$, L_2 ; $=p\text{-N(CH}_3)_2$, L_3 ; $=p\text{-OH}$, L_4 ; $=p\text{-NO}_2$, L_5 .

Experimental

Reagent grade metal salts and organic solvents were generally used.

The dibasic *Schiff* bases were prepared by refluxing *o*-phenylenediamine and aromatic aldehydes (in 1 : 2 ratio) in absolute ethanol. The solid *Schiff* base was filtered off and recrystallized from ethanol. The structures of the different dibasic *Schiff* bases were confirmed by elemental analyses.

Preparation of Metal Complexes

The general synthetic procedure used involved dissolution of 1.0 mmol of the *Schiff* base and 0.5 mmol of the metal salt [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] in the least amount of absolute ethanol. Then both the *Schiff* base and the metal salt solutions were mixed and the resulting solution was refluxed for ~ 3 h. Subsequently, the solution was concentrated to a small volume and the solid complex produced was filtered off, washed with ethanol and stored in a desiccator over dry silica gel. Several trials were made to isolate the solid Co(II) and Ni(II) complexes of L_2 , however, all experiments failed.

Due to the sparingly soluble character of L_5 in ethanol its complexes were synthesized in dioxane.

Preparation of Solutions

10^{-3} M stock solutions of the *Schiff* bases (L_1 – L_5) as well as of metal salts were prepared by dissolving the accurately weighed amount of each in absolute ethanol. In case of L_5 dioxane was used as a solvent. The metal ion solutions were standardized using the conventional procedures.

Characterization Studies

IR spectra of the ligands and their complexes were recorded on a Perkin-Elmer 599 B Spectrophotometer as KBr discs. UV and visible spectra were recorded on

both Unicam SP 8000 and SP 8-100 Spectrophotometers using 1-cm matched silica cells. Molar conductance measurements were performed with a PYE conductance bridge. All measurements were carried out at room temperature ($\sim 25^\circ\text{C}$).

Results and Discussion

The complexes isolated are given in Table 1. The elemental analysis data reported in this table reveal that the dianions of L_1 are coordinated to the metal ion while neutral molecules of the other ligands (L_2 – L_5) are coordinated to the metal ion. The general formulae of L_1 complexes are $[L_1M(H_2O)_2]$ where $M = \text{Co(II)}$, Ni(II) and $[\text{Cu}]$, while those of the other ligands are $[LM(H_2O)_2X_2]$ where $L = L_2$ – L_5 , $M = \text{Co(II)}$, Ni(II) and Cu(II) , $X = \text{NO}_3^-$, Cl^- or CH_3COO^- .

Molar conductivity determination of $10^{-3} M$ solutions of the complexes in ethanol or *DMF* are consistent with a non-electrolytic behaviour of these complexes (cf. Table 1). On the other hand, the measured molar conductance values for ethanolic solutions of Co(II) and Ni(II) complexes of L_5 suggest a 1:1 electrolyte character of these

Table 1. Analytical data, decomposition temperature and molar conductance values ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of the complexes

	Decomp. Temp. °C	Molar conduc- tance	Found (calculated)	
			%C	%N
<i>Complexes of L₁</i>				
[(C ₂₀ H ₁₄ N ₂ O ₂)Co(H ₂ O) ₂]	> 300	1.5 ^a	58.85 (58.69)	6.42 (6.84)
[(C ₂₀ H ₁₄ N ₂ O ₂)Ni(H ₂ O) ₂]	290	1.0 ^a	58.50 (58.72)	6.70 (6.85)
[(C ₂₀ H ₁₄ N ₂ O ₂)Cu]	295	0.5 ^a	63.85 (63.57)	7.22 (7.40)
<i>Complexes of L₂</i>				
[(C ₂₀ H ₁₆ N ₂)Cu(H ₂ O) ₂ (CH ₃ COO) ₂]	> 300	2.19 ^b	57.10 (57.42)	5.40 (5.58)
<i>Complexes of L₃</i>				
[(C ₂₄ H ₂₆ N ₄)Co(H ₂ O) ₂ (NO ₃) ₂]	235	6.2 ^b	48.60 (48.90)	14.10 (14.26)
[(C ₂₄ H ₂₆ N ₄)Ni(H ₂ O) ₂ Cl ₂]	178	5.4 ^b	53.50 (53.76)	10.10 (10.45)
[(C ₂₄ H ₂₆ N ₄)Cu(H ₂ O) ₂ (CH ₃ COO) ₂]	175	7.9 ^b	56.95 (57.14)	9.35 (9.35)
<i>Complexes of L₄</i>				
[(C ₂₀ H ₁₆ N ₂ O ₂)Co(H ₂ O) ₂ (NO ₃) ₂]	195	6–6 ^a	45.10 (44.86)	10.20 (10.46)
[(C ₂₀ H ₁₆ N ₂ O ₂)Ni(H ₂ O) ₂ Cl ₂]	> 300	7.4 ^b	49.60 (49.82)	5.70 (5.81)
[(C ₂₀ H ₁₆ N ₂ O ₂)Cu(H ₂ O) ₂ (CH ₃ COO) ₂]	168	4.8 ^a	54.10 (53.98)	5.10 (5.24)
<i>Complexes of L₅</i>				
[(C ₂₀ H ₁₄ N ₄ O ₂)Co(H ₂ O) ₂ (NO ₃) ₂]	130	33.7 ^a	40.10 (40.47)	13.90 (13.16)
[(C ₂₀ H ₁₄ N ₄ O ₂)Ni(H ₂ O) ₂ Cl ₂]	180	55.6 ^a	44.65 (44.46)	10.10 (10.37)
[(C ₂₀ H ₁₄ N ₄ O ₂)Cu(H ₂ O) ₂ (CH ₃ COO) ₂]	> 300	23.1 ^b	48.50 (48.68)	9.30 (9.46)

^a Measured in ethanol.

^b Measured in *DMF*.

Table 2. *Some infrared frequencies of the Schiff bases L_1 – L_5 and their Co(II), Ni(II) and Cu(II) complexes*

Compound	Frequency (cm^{-1})		
	$\nu_{\text{O-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{phenyl C-O}}$
L_1	2 800 b*	1 620	1 280
Co(II)– L_1	3 350	1 598	1 325
Ni(II)– L_1	3 500	1 613	1 345
Cu(II)– L_1	—	1 595	1 285
L_2	—	1 622	—
Cu(II)– L_2	3 360	1 558	—
L_3	—	1 618	—
Co(II)– L_3	3 600	1 620	—
Ni(II)– L_3	3 350	1 622	—
Cu(II)– L_3	3 600	1 622	—
L_4	3 300	1 608	1 265
Co(II)– L_4	3 400	1 618	1 270
Ni(II)– L_4	3 360	1 618	1 275
Cu(II)– L_4	3 460	1 620	1 260
L_5	—	1 605	—
Co(II)– L_5	3 460	1 598	—
Ni(II)– L_5	3 395	1 530	—
Cu(II)– L_5	3 500	1 603	—

* H-bonded OH.

complexes. This behaviour can presumably be ascribed to the displacement of the monodentate NO_3^- or Cl^- ligands by ethanol molecules upon dissolution.

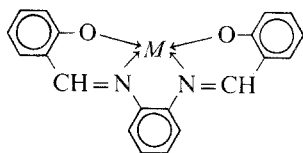
Assignment of the important IR bands, which aids in understanding of the bonding of the complexes, is presented in Table 2. The ν_{OH} band of L_1 appears as a broad one around $2\,800\text{ cm}^{-1}$. This is in consistency with the expected involvement of this group with the azomethine nitrogen through intramolecular hydrogen bonding. This band is totally disappeared in the IR spectra of the resultant L_1 complexes. Therefore, one can conclude that both the OH groups of L_1 have taken part in complex formation. The $\nu_{\text{phenyl CO}}$ of free L_1 is observed at $1\,280\text{ cm}^{-1}$. Upon complexation this band it is shifted to higher energy confirming the coordination of L_1 OH groups. However, the observed shift in this band to higher energy upon complexation can presumably be attributed to the expected high mesomeric interaction within the chelated rings (cf. structure 2).

The strong band observed in the range $1\,605$ – $1\,622\text{ cm}^{-1}$ in the IR spectra of the ligands is assigned to $\nu_{\text{C=N}}$. Upon complexation, this band is

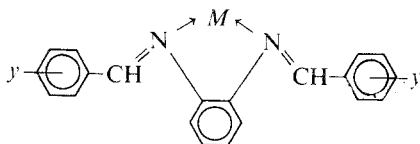
shifted to lower or higher energies confirming the coordination of the azomethine nitrogen in all the complexes.

Except in case of the $\text{Cu(II)}-L_1$ complex, the IR spectra of the complexes show a broad band in the region $3\,340-3\,600\text{ cm}^{-1}$. This suggests that water molecules are coordinated to the central metal ion. This is supported by the results of elemental analysis of the synthesized complexes (Table 1). However, the bands observed at $3\,300$ and $1\,265\text{ cm}^{-1}$ in the IR spectra of free L_4 can be assigned to $\nu_{\text{O-H}}$ and $\nu_{\text{phenyl CO}}$ respectively.

Spectrophotometric investigations in the visible region of the different complexes were performed to inspect the formation, composition and formation constants of the most stable complexes possibly formed in solution. Comparing the visible spectra of the free ligand solutions with those of the corresponding complex solutions reveals that L_1 is characterized by a high tendency towards complex formation relative to the other ligands (L_2-L_5). This is concluded from the observation that the spectrum of $3.0 \cdot 10^{-5}\text{ M}$ ethanolic solution of free L_1 differs markedly from those of its complex ethanolic solutions. The difference lies mainly in the behaviour of the longer wavelength band of free L_1 (348 nm) acquiring high red shift on complexation (33–65 nm). This behaviour can be explained as follows. The longer wavelength band observed in the spectrum of L_1 can be assigned to an intramolecular CT interaction occurring within the solute molecule^{7,8}. Thus the red shift observed in this band on complexation can be ascribed to the expected easier CT interaction in the complexed ligand ($L \rightarrow M\text{ CT}$) relative to in the free one (cf. structure 2). On the other hand, no changes are observed in the spectra of L_2-L_5 solutions upon addition of metal ion even on using high concentrations of these ligands ($\geq 5.0 \cdot 10^{-4}\text{ M}$). The observed high tendency of L_1 to form complexes relative to the other ligands can be attributed to the fact that L_1 acts as tetradentate ONON ligand where three stable chelated rings are formed (structure 2). On the other hand, the other ligands, L_2-L_5 , act as bidentate NN ligands where only one chelated ring is formed (cf. structure 3).



2



3

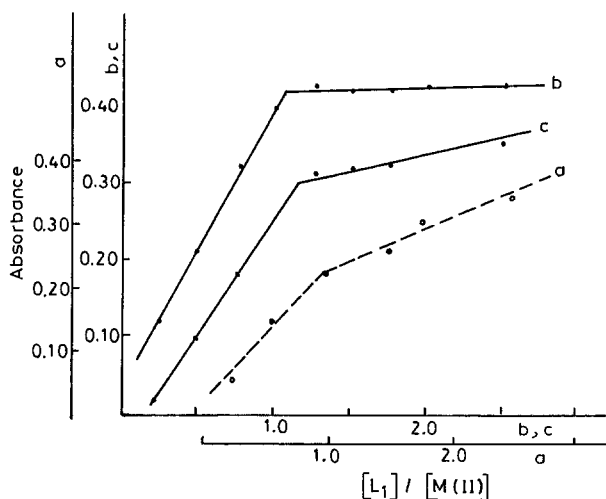


Fig. 1. Molar ratio method for metal complexes of L_1 with *a* Co(II), $\lambda = 440$ nm; *b* Ni(II), $\lambda = 420$ nm; *c* Cu(II), $\lambda = 420$ nm

The spectrophotometric methods, molar ratio⁹, and *Job's* continuous variation method¹⁰ have been applied to detect the stoichiometry of the complexes formed in ethanol solution. In these two methods, an ethanolic solution having the same concentration of ligand as that of the complex solution was used as blank. Both methods revealed 1 : 1 stoichiometry of all the complexes studied. Representative results are given in Figs. 1 and 2. The stability of the 1 : 1 L_1 complexes formed in solution was inspected by determining their apparent formation constant values utilizing the results of continuous variation method¹¹. The values obtained are $5.4 \cdot 10^5$, $8.0 \cdot 10^5$, and $2.27 \cdot 10^6$ for Co(II), Ni(II), and Cu(II) complexes, respectively, which are in agreement with the general order of stability of complexes of these metal ions^{12,13}.

Electronic Spectra of the Complexes

The UV-visible spectra of *DMF* solutions of the different complexes were recorded (Fig. 3). *DMF* was used as a solvent because some of the complexes were insoluble in ethanol and the common solvents. Furthermore, the spectra of metal complexes in *DMF* solutions exhibited no apparent differences from those recorded on mixing ethanolic solutions of both the metal ions and the ligands. This indicates that *DMF* does not act as ligand in these complexes. $\lambda_{\max}$ and $\epsilon_{\max}$ values of the different absorption bands observed are listed in Table 3. According to the

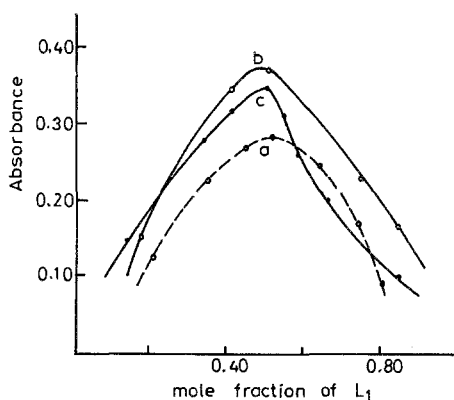


Fig. 2. Job's continuous variation plots of the metal complexes of L_1 with *a* Co(II), $\lambda = 440$ nm; *b* Ni(II), $\lambda = 420$ nm; *c* Cu(II), $\lambda = 420$ nm

Table 3. UV-visible absorption bands of various ligands and their metal complexes in DMF solutions

Complex	$\lambda_{\max}/\text{nm}$ ($\epsilon_{\max} \cdot 10^{-3}$)	Assignment
Co(II)– L_1	310 (16.60)	$\pi \rightarrow \pi^*$
	360 (9.40)	$L \rightarrow MCT$
	472 (5.80)	$L \rightarrow MCT$
Ni(II)– L_1	284 (26.17)	$\pi \rightarrow \pi^*$
	368 (38.00)	$L \rightarrow MCT$
	472 (12.60)	$L \rightarrow MCT$
Cu(II)– L_1	572 sh (1.20)	${}^3A_2g(F) \rightarrow {}^3T_1g(F)$
	300 (29.90)	$\pi \rightarrow \pi^*$
	418 (25.80)	$L \rightarrow MCT$
Cu(II)– L_2	576 (0.20)	${}^2T_2g \rightarrow {}^2Eg$
	308 (7.33)	$\pi \rightarrow \pi^*$
	376 (1.25)	$L \rightarrow MCT$
Ni(II)– L_3	305 (56.25)	$\pi \rightarrow \pi^*$
	420 (47.50)	$L \rightarrow MCT$
	570 sh (1.00)	${}^3A_2g(F) \rightarrow {}^3T_1g(F)$
Cu(II)– L_3	330 (41.17)	$\pi \rightarrow \pi^*$
	424 (6.40)	$L \rightarrow MCT$
Co(II)– L_4	284 (17.44)	$\pi \rightarrow \pi^*$
	420 (2.20)	$L \rightarrow MCT$
Ni(II)– L_4	352 (9.66)	$L \rightarrow MCT$
	570 sh (0.32)	${}^3A_2g(F) \rightarrow {}^3T_1g(F)$
	292 (21.90)	$\pi \rightarrow \pi^*$
Cu(II)– L_4	418 (6.50)	$L \rightarrow MCT$
	356 (24.70)	$L \rightarrow MCT$
Ni(II)– L_5	320 (25.60)	$L \rightarrow MCT$
	356 (11.76)	$L \rightarrow MCT$

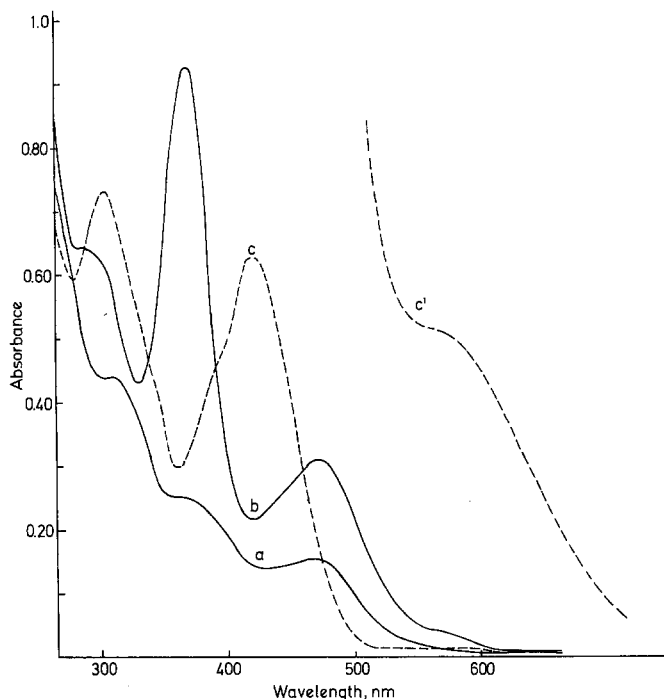


Fig. 3. UV-visible absorption spectra of DMF solutions of L_1 complexes with *a* Co(II) ($2.65 \cdot 10^{-5} M$); *b* Ni(II) ($2.44 \cdot 10^{-5} M$); *c* Cu(II) ($2.44 \cdot 10^{-5} M$); *c'* Cu(II) ($2.44 \cdot 10^{-3} M$)

work of Jaffe' and coworkers¹⁴, the band observed in the range 284–330 nm can be assigned to a transition between π -orbitals largely localized on the azomethine double bond i.e. $\pi \rightarrow \pi^*$ transition. The one or two bands appearing in the range 320–472 nm can be assigned to $L \rightarrow MCT$ transition. This assignment is based on the observation that such bands are characterized by high molar extinction coefficients ($1\,250\text{--}38\,000\text{ g mol}^{-1}\text{ cm}^2$) as well as the fact that this type of electronic transition is expected to be easier in the complexed ligands due to the positive charge of the coordinated metal ion as shown in structures 2 and 3.

Furthermore, in all the recorded spectra of the complexes studied, the longer wavelength side of the $L \rightarrow MCT$ band is associated with a broad shoulder (cf. Fig. 3) which can be attributed to a d-d electronic transition within the coordinated metal ion.

The low energy broad shoulder associated with the $L \rightarrow MCT$ band in the spectrum of the Cu(II)– L_1 complex ($\lambda_{\max} = 572\text{ nm}$, $\epsilon_{\max} = 200\text{ g mol}^{-1}\text{ cm}^2$) is indicative of a tetrahedral structure of this complex. This

suggestion is substantiated by the previous observation described by Lever¹⁵ concerning the electronic spectra of tetrahedral Cu(II) complexes where it was reported that such spectra display a single broad band of $\sim 10^2$ molar absorptivity in the range of 500–1 000 nm. Accordingly, the low energy shoulder of the Cu(II)– L_1 complex can be assigned to a $^2E_{2g} \rightarrow ^2T_{2g}$ electronic transition.

With respect to the other complexes, the low energy broad shoulder appearing in these spectra indicates a hexacoordinated configuration with low symmetry components in the ligand field, i.e. distorted octahedral geometry^{15–17}. Thus the shoulder ascertained in the spectra of Ni(II)– L_1 , – L_3 and – L_4 complexes at 572, 570 and 570 nm respectively can be assigned to a d-d electronic transition of the type $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ ¹⁶.

References

- ¹ Mahmoud M. R., Issa I. M., El-Melliegy M. S., El-Gyar S. A., Monatsh. Chem. **109**, 861 (1978).
- ² Mahmoud M. R., Issa I. M., El-Gyar S. A., Monatsh. Chem. **111**, 431 (1980).
- ³ Mahmoud M. R., El-Haty M. T., J. Inorg. & Nucl. Chem. **42**, 349 (1980).
- ⁴ Mahmoud M. R., Abd El-Hamde R., El-Haty M. T., Indian J. Chem. **19 A** (4), 345 (1980).
- ⁵ Abd El-Hamde R., Mahmoud M. R., El-Haty M. T., Bull. Soc. Chim. Belges, 891 n **11**, 963 (1980).
- ⁶ Kovacic J. E., Spectrochimica Acta **23 A**, 183 (1967).
- ⁷ Issa R. M., El-Samahy A. A., Etaiw S. H., Z. phys. Chem. **255**, 853 (1974).
- ⁸ Mahmoud M. R., El-Samahy A. A., El-Gyar S. A., Soc. Chim. de France **1981**, 424.
- ⁹ Yoe J. H., Jones A. L., Ind. Eng. Chem. (Anal. Edt.) **16**, 111 (1944).
- ¹⁰ Job P., Ann. Chim. **6**, 97 (1935).
- ¹¹ Issa I. M., Issa R. M., Abdel-Aal M. S., Egypt. J. Chem. **14**, 25 (1971).
- ¹² Grinberg A. A., Yatsimerski K. B., Bull. Acad. Sci. URSS Div. Chim. Sci. **1952**, 239.
- ¹³ Irving H., Williams R. J. P., J. Chem. Soc. **1953**, 3192.
- ¹⁴ Jaffè, H. H., Yeh S. J., Gardner R. W., J. Mol. Spectr. **2**, 120 (1958).
- ¹⁵ Lever A. B. P., Inorganic Electronic Spectroscopy, p. 357. Amsterdam: Elsevier. 1968.
- ¹⁶ Byers W., Lever A. B. P., Parish R. V., Inorg. Chem. **7**, 1835 (1968).
- ¹⁷ Day M. C., Silben J., Theoretical Inorganic Chemistry. New York-Amsterdam: Reinhold. 1969.