

Spectral, Magnetic, Thermal and Electro-Chemical Studies on Ethyl- α -(*N*-phenylthiocarbamyl)acetoacetate Complexes

R. M. El-SHAZLY

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

Received June 22, 1999; accepted August 10, 1999

Complexes of ethyl- α -(*N*-phenylthiocarbamyl)acetoacetate (HEPTA) with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) have been prepared and characterized on the basis of elemental analyses, molar conductance, magnetic moment and spectral (UV-Visible, ESR and IR) studies. IR spectra show that HEPTA behaves in a neutral or mononegative bidentate manner. A tetrahedral structure is proposed for the Co(II) complex while a square-planar structure is proposed for the Ni(II), Cu(II) and Pd(II) complexes. The thermal stability and the decomposition steps of [Ni(EPTA)₂] and [Cu(EPTA)(OAc)] were investigated with the help of TG thermograms. The Ni(II) and Co(II) complexes show two well defined electrode processes M^I/M^{II} and M^{II}/M^{III} in dimethylformamide(DMF), while the Cu(II) complex shows one electrode couple assigned to Cu(II/I).

Key words transition metal; esters; thiocarbamyl; synthesis; spectra; thermal

Sulphur compounds containing NS and NSO donor atoms and their metal complexes have been found to exhibit fungicidal, bactericidal, antiviral and antitubercular activities.^{1–3} It has been observed that small structural changes may enhance anticancer and antiviral activity of transition metal complexes.⁴

The metal complexes derived from ethyl- α -(*N*-phenylthiocarbamyl) cyanoacetate were investigated.⁵ As an extension of this work, we report herein the preparation and characterization of new metal complexes derived from ethyl- α -(*N*-phenylthiocarbamyl)acetoacetate (HEPTA). Also, their electrochemical behaviour was investigated.

Experimental

All the chemicals were of analytical grade-high purity materials (BDH).

Preparation of Ligand The ligand, ethyl- α -(*N*-phenylthiocarbamyl)acetoacetate, was synthesized according to the general published method⁶ as ethylacetoacetate (12.8 ml, 0.1 mol) was added dropwise to sodium sand (2.3 g, 0.1 mol) in 30 ml dry ether, under ice-bath cooling. Phenylisothiocyanate (10.25 ml, 0.1 mol) was added to the reaction mixture. On stirring for 24 h, a yellow precipitate is formed and separated by filtration. The formed precipitate (sodium salt of HEPTA) was dissolved in cold water, acidified with dil. HCl and filtered. The purity was checked by elemental analysis (Table 1) and IR spectra. The yield is 12 g (46%). The ligand is

readily soluble in most organic solvents and insoluble in H₂O.

Preparation of the Complexes The complexes were prepared by mixing equimolar amounts of HEPTA, (0.265 g, 1 mmol) in 30 ml absolute EtOH, and the metal acetate (0.5 mmol) in 50 ml doubly distilled water. The solid complexes that formed immediately are stirred in a water bath for 2 h. The Pd(II) complex is prepared by the same method using the calculated amount (0.09 g, 0.5 mmol) of PdCl₂ in 2 ml conc. HCl solution and precipitated by adding 0.5 g NaOAc as a buffering agent. The product in all cases was removed by filtration, washed several times with H₂O and finally dried in a vacuum desiccator over anhydrous CaCl₂.

Analyses and Measurements The metal content was determined complexometrically using semi-xylene orange (SXO) as indicator⁷ or gravimetrically in the case of Pd(II). Carbon and hydrogen analyses were carried out at the Microanalytical Unit of Mansoura University. IR spectra in the 200–4000 cm⁻¹ range were recorded on a Mattson 5000 FTIR Spectrometer as KBr discs. Solid and solution spectra were recorded on a Unicam UV₂₋₁₀₀ UV/visible spectrometer. Conductivity measurements for 10⁻³ M solution in dimethyl formamide (DMF) were made using a Tacussel conductivity bridge type CD6NG. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance and Hg[Co(NCS)₄] as a calibrant. E.S.R. spectrum of the solid Cu(II) complex was made at room temperature with a JEOL JESRE₂XG Spectrometer (100 KHz magnetic field modulation) calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH) at Tanta University. The TG graphs of the complexes were recorded between 20–1000 °C using a Shimadzu Thermogravimetric Analyzer TGA-50 with α -Al₂O₃ as a reference. The electrochemical measurements of the investigated complexes were

Table 1. Analytical and Physical Data for HEPTA and Its Complexes

Compound Empirical formula, (F.Wt)	Colour	Found (Calcd) %				μ_{eff} (BM)	Λm^a	Yield (%)
		C	H	M	X			
HEPTA C ₁₃ H ₁₅ NO ₃ S, (265.337)	yellow	58.5 (58.8)	5.9 (5.7)	—	—	—	—	46
[Cu(EPTA)(OAc)] C ₁₅ H ₁₇ NO ₃ SCu, (386.935)	yellow-green	47.0 (46.6)	4.7 (4.4)	16.0 (16.4)	—	0.79	8	84
[Co(EPTA) ₂] C ₂₆ H ₂₈ N ₂ O ₆ S ₂ Co, (587.588)	green	53.5 (53.1)	4.8 (4.8)	10.2 (10.0)	—	2.18	4	91
[Ni(EPTA) ₂] C ₂₆ H ₂₈ N ₂ O ₆ S ₂ Ni, (587.368)	red-brown	53.4 (53.2)	4.7 (4.8)	10.0 (9.99)	—	diam.	4	90
[Zn(EPTA)(OAc)] C ₁₅ H ₁₇ NO ₃ SZn, (388.775)	white	46.5 (46.3)	4.6 (4.4)	16.3 (16.1)	—	diam.	10	80
[Cd(EPTA) ₂] C ₂₆ H ₂₈ N ₂ O ₆ S ₂ Cd, (641.068)	pale-yellow	49.0 (48.7)	4.7 (4.4)	17.2 (17.5)	—	diam.	5	77
[Pd(EPTA)Cl ₂] C ₁₃ H ₁₅ NO ₃ SPdCl ₂ (442.651)	orange	35.5 (35.3)	3.6 (3.1)	24.1 (24.0)	15.7 (16.0)	diam.	7	87

a) ohm⁻¹ cm⁻² mol⁻¹.

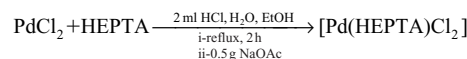
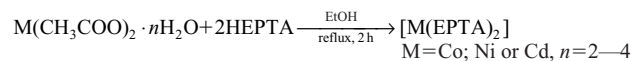
Table 2. IR. Spectral Bands (cm^{-1}) of Ethyl- α -(*N*-phenylthio-carbamyl)acetoacetate (HEPTA) and Its Metal(II) Complexes

Compound	$\gamma(\text{NH})$	$\gamma(\text{C}=\text{O})_{\text{ester}}$	$\gamma(\text{C}=\text{O})_{\text{k}}$	$\gamma(\text{C}=\text{S})$	$\gamma(\text{M}-\text{O})$	$\gamma(\text{M}-\text{S})$
HEPTA	3420	1736	1657	810	—	—
[Co(EPTA) ₂]	3435	1736	1642	—	430	370
[Ni(EPTA) ₂]	3457(w)	—	1657	792	438	365
[Cu(EPTA)(OAc)]	3437	1733	—	710	435	360
[Zn(EPTA)(OAc)]	3441	1730(w)	1630	—	415	325
[Cd(EPTA) ₂]	3464	1736	1630	—	390	315
[Pd(HEPTA)Cl ₂]	3483	1707	1644	810	360	—

carried out in DMF in the presence of tetramethylammonium bromide as supporting electrolyte. The electrochemical cell assembly consists of Ag/AgCl as reference electrode, platinum wire of 0.5 mm diameter as working electrode and glassy carbon electrode (GCE) as auxiliary electrode. The CV measurements were carried out on a potentiostat wave generator (Oxford electrodes) equipped with Phillips PM 8043 X-Y recorder.

Results and Discussion

The complexes were prepared according to the following equations:



The analytical and physical data for the isolated solid complexes are listed in Table 1. The complexes are quite stable in air and insoluble in most common organic solvents but easily soluble in DMF. Their molar conductivities at 25 °C lie in the range associated with non-electrolytes.⁸⁾ Molecular weight determinations confirm the monomeric nature of the complexes.

IR Spectral Studies In Table 2 are listed the IR assignments of the bands that undergo significant change on coordination of ethyl- α -(*N*-phenylthiocarbamyl) acetoacetate. Four possible forms (Fig. 1, structures a—d) of HEPTA are expected; in fact its IR spectrum shows the characteristic bands (I—IV) of thioamide and the carbonyl bands of both ester and ketone revealing the keto/thio keto form (a) in the solid state. The spectrum exhibits bands at 3420, 1736, 1657 and 810 cm^{-1} attributed to $\gamma(\text{NH})$, $\gamma(\text{C}=\text{O})_{\text{ester}}$, $\gamma(\text{C}=\text{O})_{\text{k}}$ and $\gamma(\text{C}=\text{S})$ vibrations, respectively. The suggested form is also supported by the absence of any bands due to $\gamma(\text{SH})$ and $\gamma(\text{OH})$ vibrations.

Structure 1 in Fig. 2 is proposed for [Co(EPTA)₂], [Zn(EPTA)(OAc)] and [Cd(EPTA)₂]. Coordination of the carbonyl group causes $\gamma(\text{C}=\text{O})_{\text{k}}$ to shift by 20—30 cm^{-1} to lower wave numbers. The loss of the proton from the CH attached to the thio keto group is confirmed from the disappearance of thioamide band IV, $\gamma(\text{C}=\text{S})$, with the appearance of new bands at —670 cm^{-1} due to $\gamma(\text{C}=\text{C})$ and $\gamma(\text{C}-\text{S})$ vibrations, respectively. Coordination of both oxygen and sulfur is also consistent with the presence of $\gamma(\text{M}-\text{O})$ ⁹⁾ and $\gamma(\text{M}-\text{S})$ ^{10,11)} vibrations at 390—430 and 315—370 cm^{-1} , respectively.

In the Ni(II) complex, the ligand chelates as in structure 2 (Fig. 2) where the thioamide IV band is shifted by 18 cm^{-1} to lower wave number indicating its coordination. The enoliza-

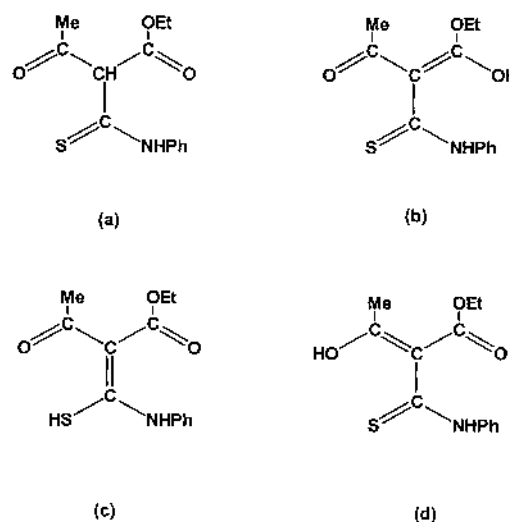


Fig. 1. Possible Structures of the Ligand

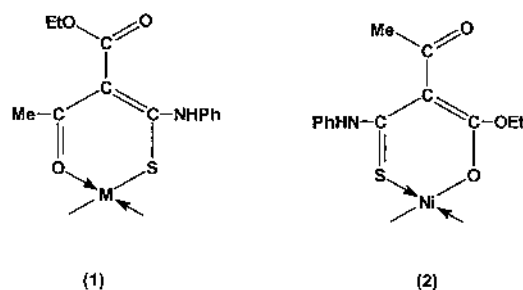


Fig. 2

tion of the carbonyl of the ester group is confirmed by the disappearance of $\gamma(\text{C}=\text{O})$ observed at 1736 cm^{-1} in the uncomplexed ligand. Bands at 365 and 438 cm^{-1} have been assigned to $\gamma(\text{M}-\text{S})$ and $\gamma(\text{M}-\text{O})$ vibrations, respectively.

The behaviour of HEPTA in its chelation with the Cu(II) ion is different. The enolization is taken through the ketonic carbonyl of HEPTA as in structure 3 (Fig. 3). The only difference is the disappearance of the band at 1657 cm^{-1} in the uncomplexed ligand. The coordination through oxygen and sulfur is supported by the presence of $\gamma(\text{M}-\text{O})$ and $\gamma(\text{M}-\text{S})$ at 455 and 360 cm^{-1} , respectively. The acetato complexes show two weak bands at *ca.* 1555 and *ca.* 1375 cm^{-1} assigned to γ_{s} OAc and γ_{as} OAc vibrations, respectively. The difference (*ca.* 180 cm^{-1}) between the two bands may suggest the bidentate nature¹²⁾ of the acetato group.

HEPTA chelates in the neutral form (a) in its reaction with PdCl₂. The chelation is carried out through the two carbonyl

groups as shown in structure 4 (Fig. 3) where the two bands at 1736 and 1657 cm^{-1} in the uncomplexed molecule are shifted by 15–30 cm^{-1} to lower wave numbers. The band at 360 cm^{-1} , due to $\gamma(\text{M}-\text{O})$, confirmed the mode of chelation. The other characteristic bands for the NH and the thioamides are more or less unshifted. The different behaviours of the ligand towards the different metal ions are mainly due to the ability of the ligand to chelate through its different forms.

In the previous work⁵⁾ on ethyl- α -(*N*-phenylthiocarbamyl)-cyanoacetate, the ligand preferred to coordinate with all the studied metal ions in the thiol form because it exists mainly in this form even in the solid state.

Magnetic, Electronic and ESR Spectral Studies Listed in Table 3 are the band maxima of the solid state and solution (DMF) electronic transitions for HEPTA and its metal (II) complexes. Omitted from the table are the higher energy $\pi \rightarrow \pi^*$ transitions (*ca.* 40000 cm^{-1}) which are not altered on complex formation. The $n \rightarrow \pi^*$ transitions associated with the thioamide and carbonyl functions of HEPTA are found at 33780, 31850 and 28490 cm^{-1} in DMF solution with $\log \epsilon = 4.088, 4.086$ and 4.218 , respectively. These bands are shifted to higher frequencies in nujol with the observation that the last one has been resolved into two peaks. The spectra of complexes generally show the higher energy band (33780 cm^{-1}) unshifted. The lower energy $n \rightarrow \pi^*$ in the ligand is apparently shifted to higher energy in the spectra of Ni(II), Cu(II) and Zn(II) complexes and not observed in the Co(II) complex. Additional bands in the region 25000–27000 cm^{-1} are due to $S_{(\pi)} \rightarrow M$ charge transfer bands.¹³⁾

The electronic spectrum of the Co(II) complex exhibits one main band at 16800 cm^{-1} in nujol attributed to the ${}^4A_2 \rightarrow {}^4T_1$ (P) transition, *i.e.* v_3 , in the tetrahedral ligand field. This

band is also observed in DMF solution at 16780 cm^{-1} with two shoulders at 17035 and 16530 cm^{-1} ; the splitting may be due to the transitions to 4B_1 and 4B_2 states.¹⁴⁾ Its magnetic moment value (2.18 BM) is lower than that reported for tetrahedral structure around the Co(II) ion. This subnormal value may be due to lower symmetry¹⁵⁾ or due to a non orbital contribution to the magnetic moment. It is also suggested that the strong Co-S bond may reduce the magnetic moment value.

The electronic spectrum of the Ni(II) complex shows two bands at 21270 and 17210 cm^{-1} , in DMF solution, which may be due to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, in a square planar geometry.¹⁶⁾ In the spectrum recorded in nujol, the first band is resolved into two bands at 21690 and 20490 cm^{-1} where the last band is shifted to higher energy. The diamagnetic nature of this complex supports the square planar geometry. Also the Pd(II) complex is diamagnetic indicating a square planar geometry as expected for a d^8 metal ion.¹⁷⁾

The magnetic moment (0.79 BM) measured for [Cu(EPTA)(OAc)] is lower than the value reported for the spin only moment (1.73 BM) measured for Cu(II) with one unpaired electron. The anomalous moment may be due to spin-spin interaction in the crystalline state. The electronic spectrum of this complex shows two broad band in DMF solution at 16370 cm^{-1} , with $\log \epsilon = 1.57$, and 16625 cm^{-1} (sh) consistent with square planar stereochemistry¹⁸⁾ and assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions.

In order to obtain further information about the stereochemistry and to determine interaction in [Cu(EPTA)(OAc)], the X-band ESR spectrum in the solid state was recorded at room temperature. The isotopic signal at $g = 2.104$ is comparable to recently studied complexes of Cu(II) with square-planar Cu(II) species.¹⁹⁾

Thermal Studies The TG thermograms of [Ni(EPTA)₂] show a thermal stability up to 163 °C after which two main decomposition steps are observed. The first step in the range 163–267 °C which is accompanied with a weight loss of 61.22% corresponds to the removal of two PhNH+MeCO+OEt (Calcd 61.37%). One undefined step at 267–359 °C is observed corresponding to the removal of the rest of the carbons as CO₂. The second decomposition step in the range 359–692 °C is characterized by a weight loss of 14.9% attributed to the conversion of NiS leaving NiO comprising 13.0% of the initial mass. This agrees well with the elemental analysis (Table 1).

In order to confirm the presence of the acetate group and

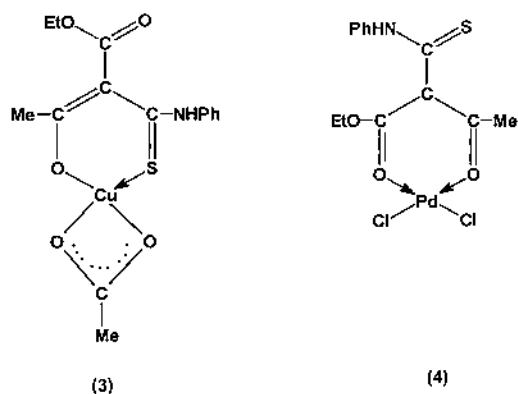


Fig. 3

Table 3. Solid State and Solution (DMF) Electronic Spectra (cm^{-1}) of Ethyl- α -(*N*-phenylthiocarbamyl)cyanoacetate (HEPTA) and Its Metal (II) Complexes

Compound	State	Intraligand bands	Charge transfer bands	d-d Bands
HEPTA	DMF	33780 (4.088), 31850 (4.986), 28490 (4.218)	—	—
	Solid	35090, 32050, 28990, 27625	—	—
[Co(EPTA) ₂]	DMF	33330 (4.15)	—	17035 (sh), 16780 (sh), 16530 (2.24)
	Solid	33330, 26810	24330	16800
[Ni(EPTA) ₂]	DMF	33360 (sh), 30670 (sh), 29410 (sh), 28730 (4.61)	—	21270, 17210
	Solid	32570, 30960, 29070, 27320	—	21690, 20490, 19760
[Cu(EPTA)(OAc)]	DMF	33330 (sh), 30960 (4.09), 28900 (4.16), 27550 (sh)	—	16370 (1.57), 6625 (sh)
	Solid	35090, 33110, 30960	25905, 22675	17360
[Zn(EPTA)(OAc)]	DMF	33110, 28900	—	—
[Cd(EPTA) ₂]	DMF	28170	25770, 23640	—

Table 4. Cyclic Voltammetric Data for the Investigated Complexes in DMF at $100 \text{ mV} \cdot \text{s}^{-1}$ Scan Rate

Type of complex	First electrode couple			Second electrode couple		
	$-E_c(\text{V})$	$-E_a(\text{V})$	$\Delta E_p(\text{V})$	E_c	E_a	ΔE_p
[Ni(EPTA) ₂]	-0.80	-0.30	0.50	+0.30	1.06	0.76
[Co(EPTA) ₂]	-0.80	-0.53 ^{a)}	0.27	+0.36	0.60	0.24
[Cu(EPTA)(OAc)]	-0.6	-0.1	0.50	—	—	—
[Zn(EPTA)(OAc)]	-0.46	+0.34	0.80	—	—	—

a) III defined.

Table 5. Effect of Scan Rate ($50\text{--}200 \text{ mV} \cdot \text{s}^{-1}$) on the Electrochemical Behaviour of Copper (II) Complex

Scan rate	$E_a(\text{V})$	$E_c(\text{V})$	$\Delta E_p(\text{mV})$
50	-0.612	-0.152	460
100	-0.6	-0.10	500
200	-0.580	-0.110	578

to know the thermal stability of the complexes isolated from metal acetate, [Cu(EPTA)(OAc)] is taken as an example. The TG thermograph of this complex shows thermal stability up to 110°C after which three decomposition steps are observed. The first one in the range $110\text{--}263^\circ\text{C}$ with a weight loss of 46.27% corresponds to the elimination of $\text{PhNH} + \text{OEt} + \text{Me}$ (Calcd 46.66%). The second step with a weight loss of 16.06% corresponds to the removal of the chelated acetato group (Calcd 15.28%). The third step with 9.17% weight loss is attributed to the removal of the remaining carbons (Calcd 9.33%). The final product (CuO) has 20.65% residual which agrees with the data in Table 1.

Electrochemical Studies The CV data of the complexes are summarized in Table 4. Two well defined cathodic waves at -0.8 and 0.3 V coupled with two anodic waves at -0.3 and 1.06 V versus Ag/AgCl electrode are observed for the Ni(II) complex at $100 \text{ mV} \cdot \text{s}^{-1}$. The two electrode couples are safely assigned to irreversible couples $\text{Ni}^{\text{I/II}}$ and $\text{Ni}^{\text{II/III}}$, respectively. The ratio of the peak currents of the reverse (i_r) to forward (i_f) scan remains constant (0.94) at slow and high scan rates as expected for $\text{Ni}^{\text{II/I}}$ species. Increasing the scan rate ($\geq 500 \text{ mV} \cdot \text{s}^{-1}$) increases the cathodic-anodic peak separation and the ratio of i_r/i_f varied from 0.9—0.98 for the electrode couple $\text{Ni}^{\text{II/III}}$. The data suggest the formation of different species with varying scan rate or the species that formed initially in the reduction process changed to some other forms that are not reoxidized at the same potential.

The CV of the Cu(II) complex displayed a well defined cathodic wave at -0.6 V coupled with an anodic wave at

$100 \text{ mV} \cdot \text{s}^{-1}$ in the potential range $-1.0\text{--}1.0 \text{ V}$. The electrode couple is assigned to $\text{Cu}^{\text{I/II}}$. The effect of scan rate (Table 5) on the CV of the Cu(II) complex confirms the formation of different complex species. The assignment of this electrode couple was confirmed by controlled potential electrolysis on the electrode potential of the couple. The value of n was found to be 1.01—1.21 establishing one electron transfer for each electrode couple.

In the CV of the Co(II) complex, two well defined cathodic waves at -0.80 and 0.36 V coupled with two anodic waves at -0.53 and 0.6 V are observed. Controlled potential electrolysis at -0.90 and 0.60 V showed one mole electron/mole of the complex for each couple. Therefore, the two electrodes are possibly assigned to $\text{Co}^{\text{I/II}}$ and $\text{Co}^{\text{II/III}}$ with $E^\circ = -0.665$ and 0.48 V , respectively, at $100 \text{ mV} \cdot \text{s}^{-1}$. No significant changes were observed on the peak potentials, cathodic-anodic peak separation and the ratio of i_r/i_f on changing scan rate from 50 to $500 \text{ mV} \cdot \text{s}^{-1}$.

The CV of the Zn(II) complex revealed an irreversible electrode couple with cathodic wave at -0.46 coupled with an anodic wave at 0.34 V at $100 \text{ mV} \cdot \text{s}^{-1}$. The two waves are assigned to the redox behaviour of the ligand.

Acknowledgement The author is grateful to Prof. M.S. El-Shahawi for help with the cyclic voltammetric studies.

References

- 1) Ali M., Livingston S. E., *Coord. Chem. Rev.*, **13**, 101—132 (1974).
- 2) Cleare M. J., *Coord. Chem. Rev.*, **12**, 349—405 (1974).
- 3) Williams D. R., *Chem. Rev.*, **72**, 203—213 (1972).
- 4) Das M., Livingston S. E., *Inorg. Chem. Acta*, **19**, 5—10 (1976).
- 5) El-Shazly R. M., Bekheit M. M., Abu El-Reash G. M., *Transition Met. Chem.*, **16**, 492—494 (1991).
- 6) Worrall D. E., *J. Amer. Chem. Soc.*, **42**, 1055—1061 (1922).
- 7) Vogel A. I., *Quantitative Inorganic Analysis*, Longmans, London, 1961.
- 8) Geary W. J., *Coord. Chem. Rev.*, **7**, 81—122 (1971).
- 9) Specca A. N., Karayannis N. M., Pytrewski L. L., *Inorg. Chim. Acta*, **9**, 87—93 (1974).
- 10) Ferraro J. R., *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, 1971.
- 11) El-Asmy A. A., Mounir M., *Transition Met. Chem.*, **13**, 143—145 (1988).
- 12) El-Asmy A. A., Babaqi A. S., Shaibi Y. M., Al-Ansi T. Y., *Bull. Soci. Chim. Fr.*, **3**, 428—431 (1988).
- 13) West D. X., Ives J. S., Baln G. A., Liberta A. E., Martinez J. V., Ebert K. H., Ortega S. H., *Polyhedron*, **16**, 1895—1905 (1997).
- 14) El-Asmy A. A., Shaibi Y. M., Shedaiwa I. M., Khattab M. A., *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 461—481 (1990).
- 15) El-Asmy A. A., Al-Ansi T. Y., Amin R. R., Mounir M., *Polyhedron*, **9**, 2029—2034 (1990).
- 16) Singh S., Yadava B. P., Aggarwal R. E., *Indian J. Chem.*, **23A**, 441—443 (1984).
- 17) Bhava N. S., Kharat R. B., *J. Inorg. Nucl. Chem.*, **42**, 977—983 (1980).
- 18) Sacconi L., *Transition Met. Chem., Ser. Advan.* **4**, 199—298 (1968).
- 19) Beraldo H., West D. X., *Transition Met. Chem.*, **22**, 294—298 (1997).