REACTIVITY OF CERTAIN BIOLOGICALLY IMPORTANT AZOLES AND MORPHOLINE TOWARDS Ni(II) AND Cu(II) COMPLEXES OF o-HYDROXYACETOPHENONEETHANOLIMINE AND N-SALICYLIDENE DERIVATIVES

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حضر عدد من المتراكبات مختلطة الليجندات للنيكل والنحاس الثنائيين مع قواعد شيف أرثوهيدروكسى أسيتوفينون إيثانول إمين وسليسيليدين أرثو إمينو فينول وسليسيلدين أرثو تولودين وكذلك مع بعض الازولات والمورفولين. درست المتراكبات بإستخدام أطياف المنطقة المرئية والفوق بنفسجية والمنطقة تحت الحمراء وأيضا بالقياسات المغناطيسية.

A number of mixed ligand complexes of Ni(II) and Cu(II) containing the Schiff bases: o-hydroxyacetophenoneethanolimine (OHAE), N-salicylidene-o-iminophenol (SOP) and N-salicylidene-o-toluidine (SOT) as well as morpholine or the azoles: 2-aminothiazole, benzothiazole and 2-methylbenzothiazole has been prepared and characterized. The IR, UV-VIS spectra and magnetic moment measurements of the complexes were discussed.

INTRODUCTION

Azomethine derivatives and their metal complexes perform an important role in biological systems.^{1&2} Many Schiff bases exhibit antiviral and antimicrobial activity³ and are used as mimetic systems for enzyme models⁴ besides their

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importance in pharmaceutical technology.⁵

Furthermore, the increasing interest in the chemistry of five membered heterocyclic molecules and their metal complexes is due to their biological and pharmaceutical importance.6&7 It was recently reported that of 2complexes aminothiazole exhibit some significant in vivo antitumor activitry against P388 leukemia.849 In view of this importance of Schiff bases and thiazoles and in view of our interest in the coordination chemistry of these Lewis bases,¹⁰⁻¹² the present paper deals with the preparation and characterization of ternary complexes of Ni(II) and Cu(II) comprising certain Schiff bases and thiazoles or morpholine.

EXPERIMENTAL

All solvents and reagents used in this work were of analytical grade. The ligands used in this work were procedures.¹³⁻¹⁵ reported Their prepared according literature names, notations and structures are given in Table 1. The following binary complexes were prepared as described in the literature:¹³⁻¹⁶ aqua(ohydroxyacetophenoneethanoliminato) copper(II) (decomp. point 135°, light blue), aqua(N-salicylidene-o-iminophenolato)nickel(II) (decomp. point 190°, beige), aqua(N-alicylidene-oiminophenolato)copper(II) (decomp. point 210°, green) and bis(Nsalicylidene-o-toluidine)copper(II) (decomp. point 297°, yellowish brown). The mixed ligand complexes were prepared as follows:

Names	Notation	Structure
o-Hydroxyacetophenone- ethanolimine	(OHAE)	CH ₃ OH
N-Salicylidene-o-iminophenol	(SOP)	CH=N OH HO
N-Salicylidene-o-toluidine	(SOT)	CH=N OH H ₃ C

Table 1: Names, notations and structures of the ligands under investigation.

(i) Preparation of (o-hydroxyacetophenoneethanoliminato)(2aminothiazole)copper(II), [Cu(OHAE) (2-Atz)], (ohydroxyacetophenoneethanoliminato)(benzothiazole)copper(I I), [Cu(OHAE) (Btz)], (ohydroxyacetophenoneethanoliminato)(3-methyl-2-selenoxothazothiazole)copper (II), [Cu(OHAE)(3-Msbbtz)] and (ohydroxyacetophenoneethanoliminato)(thiabendazole)copper (II)monohydrate, [Cu(OHAE) (Tbdz)].H₂O

A methanolic solution (50 ml) of [Cu(OHAE)(H₂O)] (0.012 mol) was mixed with a methanolic solution (20 ml) of 2-aminothiazole (2-Atz). benzothiaozle (Btz), 3-methyl-2selenoxobenzothiazole (3-Msbtz) or thiabendazole (Tbdz) (0.012 mol) with continuous stirring for about 15 minutes. The mixture was then heated under reflux for 3-4 h. The solution was filtered and allowed to cool, whereby brown or green precipitates were obtained. The collected solid chelates were washed with methanol and dried in air.

(ii) Preparation of (N-salicylideneo-iminophenolato)(2-aminothiazole)nickel(II), [Ni(SOP)(2-Atz)], (N-salicylidene-o-iminophenolato)(benzothiazole)nickel (II), [Ni(SOP)(Btz)], (N-salicylidene-o-iminophenolato)(2methylbenzothiazole)nickel(II), [Ni(SOP)(2-Mbtz)] and (Nsalicylidene-o-iminophenolato)-(morpholine)nickel(II), [Ni(SOP)(Morph)]

A methanolic solution (30 ml) of $[Ni(SOP)(H_2O)]$ (0.001 mol) was mixed with a methanolic solution (15

ml) of 2-aminothizole (2-Atz), benzothiazole (Btz), 2-methylbenzothiazole (2-Mbtz) or morpholine (Morph) (0.001 mol), and then the mixtures were heated under reflux for 4-5 h. Upon reduction of the mixture volume and cooling, coloured solids of the ternary complexes separated out, which were filtered and dried in air.

(iii) Preparation of (N-salicylideneo-iminophenolato)(benzothiazole)copper(II), [Cu(SOP)(Btz)]

A methanolic solution (20 ml) of $[Cu(SOP)(H_2O)]$ (0.001 mol) was mixed with a methanolic solution (20 ml) of benzothiazole (Btz) (0.001 mol) and the mixture was heated under reflux for 4-5 h. The green product was collected, washed with methanol and air dried.

(iv) Preparation of bis(N-salicylidene-o-toludine)bis-(morpholine) copper(II), [Cu(SOT)₂(Morph)₂]

An ethanolic solution (50 ml) of $[Cu(SOT)_2]$ (0.001 mol) and an ethanolic solution (20 ml) of morpholine (Morph) (0.002 mol) were mixed in a 1:2 (compelx : ligand) ratio. The mixture was refluxed on a water bath (70°) for about 3 h. The solution was filtered and allowed to cool. A pink precipitate was separated, washed with ethanol and finally dried in air.

Physical measurements

The carbon, hydrogen, nitrogen and sulfur contents of the solid

compounds were determined bv Elementar Analysensystem GmbH Vario EL. The infrared spectra of all compounds were recorded on a 470 Shimadzu infrared spectrophotometer $(4000-400 \text{ cm}^{-1})$ using KBr disks. The absorption electronic spectral measurements in the ultraviolet and visible regions were carried out as nujol mull on a UV-2102 PC Shimadzu spectrophotometer, using 1 cm matched quartz cell in the wavelength range 200-900 nm. The X-rav data were collected at room temperature (25°) on a Philips 1710 diffractometer. The patterns were run with Cu target (λ = 1.5418 Å) in the range of $2\theta = 10^{\circ} - 70^{\circ}$ with a scanning speed Magnetic of 6°/min. susceptibilities of the compounds were measured at room temperature a magnetic susceptibility using balance of the type MSB-Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants. The calibrant used was $Hg[Co(SCN)_4].$

RESULTS AND DISCUSSION

Binary complexes of Ni(II) and Cu(II) derived from o-hydroxyacetophenoneethanolimine, N-salicylideneo-iminophenol or N-salicylidene-otoluidine react readily with 2-aminothiazole (2-Atz), benzothiazole (Btz), 2-methylbenzothiazol (2-Mbtz), 3methyl-2-selenoxobenzothizole (3-Msbtz), thiabendazole (Tbdz) and morpholine (Morph) to form the corresponding ternary complexes. The reactions proceed according to the following equations: $[Cu(OHAE)(H_2O)] + L \rightarrow$ $[Cu(OHAE)(L)] + H_2O$ (1) where L = (2-Atz) (Btz) (3-Msbtz)

where L = (2-Atz), (Btz), (3-Msbtz) or (Tbdz)

$$\begin{array}{l} [\text{Ni(SOP)(H_2O)]} + L \rightarrow \\ [\text{Ni(SOP)(L)]} + H_2O \end{array}$$

(2) $I = (2-\Delta tz) \quad (Btz) \quad (2-Mbtz) \quad o$

where L = (2-Atz), (Btz), (2-Mbtz) or (Morph)

$$\begin{array}{l} [Cu(SOP)(H_2O)] + Btz \rightarrow \\ [Cu(SOP)(Btz)] + H_2O \\ (3) \\ [Cu(SOT)_2] + 2 Morph \rightarrow \\ [Cu(SOT)_2(Morph)_2] \\ (4) \end{array}$$

The resulting metal complexes can be divided into two categories according to their stoichiometric ratios, namely 1:1 in the ternary metal complexes [Cu(OHAE)(2-Atz)], [Cu(OHAE)(Btz)], [Cu(OHAE)(3-Msbtz)], $[Cu(OHAE)(Tbdz)].H_2O,$ [Ni(SOP)(2-Atz)],[Ni(SOP)(Btz)], [Ni(SOP)(2-Mbtz)], [Ni(SOP)-(Morph)] and [Cu(SOP)(Bt)] and 1:2 metal complex to ligand in [Cu(SOT)₂(Morph)₂]. The complexes are partially soluble in DMF, but sparingly soluble in alcohol, acetone and ether. Elemental analysis, colour and decomposition points of the ternary complexes are tabulated in Table 2.

		C%	H%	N%	S%	Decomp
Compound	Colour	(calc.)	(calc.)	(calc.)	(calc.)	mp/°C
Cu((OHAE)(2-Atz)]	Brown	46.48	5.26	13.38	10.00	215
		(45.80)	(4.43)	(12.32)	(9.40)	
[Cu(OHAE)(Btz)]	Green	55.57	4.31	8.14	8.92	216
		(54.31)	(4.28)	(7.45)	(8.52)	
[Cu(OHAE)(3-Msbtz)]	Yellow-	47.00	4.51	6.43	7.51	219
	ish green	(46.10)	(3.86)	(5.97)	(6.83)	
[Cu(OHAE)(Tbdz)].H ₂ O	Light	53.00	4.71	13.00	7.50	224
	green	(52.22)	(4.38)	(11.18)	(6.97)	
[Ni(SOP)(2-Atz)]	Brown	52.70	4.05	11.76	9.02	>300
		(51.92)	(3.54)	(11.35)	(8.66)	
[Ni(SOP)(Btz]	Yellow	60.00	3.53	7.50	8.61	>300
		(59.29)	(3.48)	(6.94)	(7.91)	
Ni(SOP)(2-Mbtz)]	Pale	61.01	4.04	7.20	8.10	>300
	yellow	(60.17)	(3.84)	(6.68)	(7.63)	
[Ni(SOP)(Morph)]	Deep	58.08	5.23	8.14	-	>300
	brown	(57.17)	(5.07)	(7.87)	-	
[Cu(SOP)(Btz)]	Green	59.23	3.56	7.38	8.50	>300
		(58.59)	(3.44)	(6.83)	(7.82)	
[Cu(SOT) ₂ (Morph) ₂]	Pink	67.05	5.03	9.47	-	159
		(65.65)	(6.43)	(8.51)	-	

Table 2: Colour, elemental analysis and decomposition points of the mixed ligand complexes.

IR spectra

The most important infrared spectral bands that provide the coordination sites in the formed ternary complexes are given in Table 3. The spectra of the ternary complexes display a band associated with a shoulder in the region 1590-1650 cm⁻¹ that can be attributed to v(C=N) of the azomethine group and v(C=N) of the 2-aminothiazole and benzothiazole. The v(NH₂) of 2aminothiazole and $\nu(NH)$ of morpholine are observed in the range of 3190-3370 cm⁻¹. A band appearing in the range 1200-1300 cm⁻¹ is attributed to v(C-O) phenolic. The thiazole ligands exhibit in general

v(C-S) as a sharp band in the range 650-790 cm⁻¹. Comparison of the spectra of the ternary complexes with those of the binary complexes was made. The bands associated with v(C=N) and v(C-O) phenolic of the binary complexes are observed in the range 1600-1620 and 1300-1320 cm⁻¹, respectively. No significant shifts in the positoin of these two bands in the ternary complexes could be traced. Metal-nitrogen and metaloxygen bonding display their absorptions at 460-470 and 480-490 cm⁻¹, respectively.¹⁷⁻²⁰ This is a further evidence for coordination of the metal ions through oxygen and nitrogen atoms of the ligands.

Compound	v(C=N)	ν(N-H)	v(C-O)	v(C-S)	v(M-O)	v(M-N)
Cu((OHAE)(2-Atz)]	1660 s	3290	1200 s	790	490	470
	1640 sh					
[Cu(OHAE)(Btz)]	1610 s	-	1220	750	490	460
	1620 sh					
[Cu(OHAE)(3-Msbtz)]	1600 s	-	1280	740	495	470
[Cu(OHAE)(Tbdz)].H ₂ O	1595 s	3300	1290	743	480	460
	1640 sh					
[Ni(SOP)(2-Atz)]	1620 s	3370	1300	660	490	470
	1650 sh					
[Ni(SOP)(Btz]	1620 s	-	1290	655	485	475
	1655 sh					
Ni(SOP)(2-Mbtz)]	1590 s	-	1295	720	490	476
	1620 sh					
[Ni(SOP)(Morph)]	1605 s	3300	1310	-	480	460
[Cu(SOP)(Btz)]	1610 s	-	1300	700	490	465
	1650 sh					
[Cu(SOT) ₂ (Morph) ₂]	1610 s	3190	1200	-	480	470

Table 3: IR spectral data of the complexes (cm⁻¹).

s = sharp, sh = shoulder.

Electronic spectra and magnetic measurements

The electronic spectral data of the ternary complexes in nujol mull are given in Table 4. The absorption spectra of the [Cu(OHAE)(2-Atz)], [Cu(OHAE)(Btz)], [Cu(OHAE)(3-[Cu(OHAE)(Tbdz)].H₂O, Msbtz)], [Cu(SOP)(Btz)] and [Cu(SOT)₂-(Morph)₂] ternary complexes are characterized mainly by three absorption bands in region 15,040-38,460 cm⁻¹. The broad absorption band in the range $15,040-16,580 \text{ cm}^{-1}$ is attributed to a d-d transition. The band in the 21,230-25,520 cm⁻¹ range is assigned to a charge transfer transition.^{21&22}. Furthermore, the absorption band in the range 28,33034,015 cm⁻¹ is attributed to an intraligand transition.

The electronic spectra of [Ni(SOP)(2-Atz)],[Ni(SOP)(Btz)], [Ni(SOP)(2-Mbtz)] and [Ni(SOP)-(Morph)] ternary complexes are recorded as nujol null. The d-d transitions could not be observed in the spectra of these complexes due to charge transfer tailing from UV to visible region, which precluded the assignment of the structure around the Ni(II) ion. The complexes exhibited, however, a band in the range 21,230-25,520 cm⁻¹, ascribed to a charge transfer transition.²³ The intraligand transitions are associated with the bands appearing in the ranges 27,470- $34,015 \text{ and } 37,740-38,460 \text{ cm}^{-1}$.

Compound	$v_{\rm max}~({\rm cm}^{-1})$	Band assignment	
Cu((OHAE)(2-Atz)]	15,780	d-d transition	
	23,100	Charge transfer	
	28,330	Intraligand transition	
[Cu(OHAE)(Btz)]	16,000	d-d transition	
	24,390	Charge transfer	
	32,570	Intraligand transition	
[Cu(OHAE)(3-Msbtz)]	16,580	d-d transition	
	24,330	Charge transfer	
	28,330	Intraligand transition	
[Cu(OHAE)(Tbdz)].H ₂ O	15,040	d-d transition	
	23,700	Charge transfer	
	33,440	Intraligand transition	
[Ni(SOP)(2-Atz)]	23,750	Charge transfer	
	(27,470), (37,590)	Intraligand transition	
[Ni(SOP)(Btz]	23,200	Charge transfer	
	(32,470), (37,740)	Intraligand transition	
Ni(SOP)(2-Mbtz)]	23,700	Charge transfer	
	(33,330), (38,460)	Intraligand transition	
[Ni(SOP)(Morph)]	24,940	Charge transfer	
	(32,790), (37,740)	Intraligand transition	
[Cu(SOP)(Btz)]	15,650	d-d transition	
	21,230	Charge transfer	
	33,560	Intraligand transition	
[Cu(SOT) ₂ (Morph) ₂]	16,390	d-d transition	
_	25,520	Charge transfer	
	34,015	Intraligand transition	

Table 4: Electronic spectral data of the ternary complexes (cm⁻¹).

The above data can be discussed as follows:

(i) For the copper complexes, the position of their d-d band in the range 15,040-16,580 cm⁻¹ is found to be similar to that of a d-d band exhibited by analogous imidazole, benzothiazole and benzoxazole complexes.^{24&25} This may indicate coordination of the azoles and morpholine in the prepared copper complexes

through the nitrogen atoms. This is further supported from the above mentioned assignment of the IR band in the region 460-470 cm⁻¹ as v(Cu-N).

A further confirmation of this coordination site in these complexes comes from a study done by Y. Muto *et al.*²⁶ on a series of Cu(II) complexes having the general formula $[Cu(Ac)_2L]$ (where Ac= acetate and L represents some azoles derivatives). It

was reported that in this series the nitrogen atom of the ligand L is most probably the donor atom.

(ii) A similar coordination mode is expected for the azoles and morpholine in the Ni(II) complexes (vNi-N,460-470 cm⁻¹, Table 3). Aly *et al.*¹⁰ prepared a number of Ni(II) mixed ligand complexes of alkylxanthate with benzothiazole, benzoxazole and morpholine in which these azoles and morpholine coordinate via the nitrogen atom.

Recently a mixed ligand complex of Co(III)-N,N'-disalicylidene-1,2phenylenediamine dianion and morpholine was prepared where the latter coordinates through its nitrogen atom. Crystal structure determination confirmed this type of bonding.²⁷

The effective magnetic moment values for the invetigated Ni(II) complexes are in the range 3.4-3.6 B.M., which may indicate their tetrahedral structure. These values are lower than expected value (4.1 B.M.), probably due to the effect of covalency or distortion from the tetrahedral structure.²⁸ The Cu(II) complexes display, however, effective magnetic moment values in the range 1.62-1.79 B.M. It is asumed that the

copper complexes adopt a tetragonal geometry which is produced probably through the interaction of the copper in the complexes with adjacent ligands of neighboring complex molecules.

X-ray powder diffraction

The compounds [Cu(OHAE)-(Tbdz)].H₂O, [Ni(SOP)(2-Atz)], [Ni(SOP)(Btz)], [Cu(SOP)(Btz)] and [Cu(SOT)₂(Morph)₂] were studied by X-ray powder diffraction. In Table 5, the (d) spacing, (2θ) and the relative intensities of the lines in the powder diffraction pattern of [Cu(OHAE)-(Tbdz)].H₂O are tabulated. The patterns of the complexes display lines indicating that the complexes are more or less crystalline.

Tenative structures

Although it was difficult to assign the structures of the complexes from the electronic spectral data due to the great broadness of the d-d transition band in the copper complexes and the absence of this band in the nickel complexes, the magnetic moment data indicate the tetrahedral structure of the Ni(II) complexes and the tetragonal structure of the Cu(II) complexes. In the following are the tentative structures of the complexes:

(20)	(d) spacing	Relative intensity (I/I ₂)	(20)	(d) spacing	Relative intensity (I/I ₂)
10.52	8.409	15	37.85	2.377	37
11.08	7.986	17	38.68	2.328	23
12.70	6.969	28	39.88	2.26	21
14.84	5.969	16	43.08	2.1	22
16.54	5.36	52	44.48	2.037	27
17.55	5.054	46	45.32	2.001	18
18.24	4.863	23	45.52	1.993	19
21.03	4.224	100	46.00	1.973	20
22.01	4.039	19	48.44	1.879	19
22.64	3.927	14	49.0	1.858	21
23.91	3.721	27	50.32	1.813	19
24.89	3.578	38	51.52	1.774	20
25.52	3.49	29	52.56	1.74	18
26.31	3.387	59	55.36	1.717	19
27.25	3.273	24	54.16	1.693	20
27.72	3.218	19	54.56	1.682	18
28.76	3.104	19	54.68	1.679	19
29.44	3.034	16	56.24	1.636	19
31.84	2.81	29	56.64	1.625	19
32.40	2.763	19	60.44	1.532	19
33.28	2.692	23	61.76	1.502	17
34.24	2.619	18	62.36	1.489	19
35.56	2.525	23	62.99	1.476	22
37.04	2.427	20	65.08	1.433	18

Table 5: X-ray powder diffraction data for [Cu(OHAE)(Tbdz)].H2O.



Cu((OHAE)(2-Atz)]



[Cu(OHAE)(Btz)]



[Cu(OHAE)(3-Msbtz)]



[Ni(SOP)(2-Atz)]



[Cu(OHAE)(Tbdz)].H₂O



[Ni(SOP)(Btz]



Ni(SOP)(2-Mbtz)]





[Cu(SOP)(Btz)]



[Ni(SOP)(Morph)]



[Cu(SOT)₂(Morph)₂]

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REFERENCES

- S. M. El-Kousy, F. A. Ali, A. M. Donia and F. A. El-Said, Egypt. J. Pharm. Soc., 28, 107 (1987).
- 2- C. P. Raptopoulou, A. N. Papadopoulou, D. A. Malamatari, E. Loannidis, G. Molsidis, A. Terzis and D. P. Kessissoglou, Inorg. Chim. Acta, 272, 283 (1998).
- 3- R. Pignatello, A. Panicol, P. Mazzone, M. Pinizzotto, A. Garozzo and P. Furneri, Eur. J. Med. Chem., 29, 781 (1994).
- 4- L. Guofa, S. Tongshum and Z. Yonghian, J. Mol. Struct., 412, 75 (1997).



- 5- F. Bergant, S. Pacar, S. Ghosh, S. K. Chattopadhyay and G. Sava, Anti Cancer Res., 13, 1007 (1993).
- 6- L. S. Goodman and A. Gilman, "The Pharmacological Basis of Therapeutics", 5th Ed., Macmillan, New York (1975).
- 7- R. lackhan and B. Ternai, Adv. Heterocy. Chem., 17, 99 (1974).
- 8- B. K. Keppler, "Metal Complexes in Cancer Themotherapy", VCH, Weinheim (1993).
- 9- P. Mura, F. Piccioli, C. Gabbianai, M. Camalli and L. Messori, Inorg. Chem., 44, 4897 (2005).
- 10- A. A. M. Aly, M. S. El-Meligy, A. S. A. Zidan and M. El-Shabasy, Synth. React. Inorg. Met.-Org. Chem., 17, 257 (1987).
- A. A. M. Aly, M. S. El-Meligy, A. S. Zidan and M. El-Shabasy, An. Quim., 86, 19 (1990).
- 12- A. H. Osman, A. A. M. Aly, M. Abd El-Mottaleb and G. A. H. Gouda, Bull. Korean Chem. Soc., 25, 45 (2004).
- P. R. Shukla, V. K. Singh and A. M. Jaiswal, J. Indian Chem. Soc., LX, 321 (1983).
- 14- A. P. Mishra, M. Khare and S. K. Gautam, Synth. React. Inorg. Met.-Org. Chem., 32, 1485 (2002).
- 15- A. M. Shallaby, M. M. Mostafa and M. M. Bekheit, Indian J. Chem., 17A, 516 (1979).

- 16- B. A. Jani and P. K. Bhattacharya, J. Indian Chem. Soc., LVIII, 207 (1981).
- 17- a) H. M. El-Tabl, F. A. El-Saied and M. I. Ayad, Synth. React. Inorg. Met.-Org. Chem., 32, 1245 (2002). b) A. A. Abou-Hussen, N. M. El-Metwally, E. M. Saad and A. A. El-Asmy, J. Coord. Chem., 58, 1735 (2005).
- 18- M. X. West, H. Gebremedhin, T. J. Romack and A. E. Liberta, Transition Met. Chem., 19, 426 (1994).
- 19- S. I. Valentina and P. A. Mikhail, Inorg. Chim. Acta, 189, 259 (1991).
- 20- a) N. T. Madhu and P. K. Radhakrishnan, Transition Met. Chem., 25, 287 (2000). b) N. M. El-Metwally, I. M. Gabr, A. A. El-Asmy and A. A. Abou-Hussen, Transition Met. Chem., 31, 71 (2006).
- 21- S. Kumar and N. K. Kaushik, Inorg. Nucl. Chem., 11, 43 (1981).
- 22- S. Wang and S. Liu, Inorg. Chem. Acta, 196, 231 (1992).
- 23- a) A. I. El-Said, A. S. A. Zidan, M. S. El-Meligy, A. A. M. Aly and O. F. Mohammed, Synth. React. Inorg. Met.-Org. Chem., 30, 1373 (2000). b) A. A. A. Abu-Hussein, J. Coord. Chem., 59, 157 (2006).
- 24- S. V. Deshpande and T. S. Srivastava, Polyhedron, 2, 261 (1983).

- 25- A. A. Mohamed, A. A. M. Aly and M. El-Shabasy, Croat. Chim. Acta, 59, 509 (1986).
- 26- Y. Muto, T. Tokii, K. Chijiwa and M. Kato, Bull. Chem. Soc. Japn., 57, 1011 (1984).
- 27- M. Amirnasr, K. J. Schenk, A. Gorji and R. Vafazadeh, Polyhedron, 20, 695 (2001).
- 28- L. Sacconi, R. Cini, M. Ciampalini and F. Maggo, J. Am. Chem. Soc., 82, 3487 (1960).