

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa www.sciencedirect.com



ORIGINAL ARTICLE

γ -Irradiation and characterization of synthesized methoxybenzylpyrimidine formimidate Schiff-base and some metal-complex derivatives



R.O. Aly ^{a,*}, R.S. Farag ^b, M.M. Hassan ^b

^a National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

^b Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt

Received 31 March 2011; accepted 10 September 2011 Available online 20 September 2011

KEYWORDS Schiff-base; Metal-complex; Spectral analysis; γ-Irradiation; Antimicrobial activity	Abstract A Schiff-base, I, was prepared by the condensation reaction between the amine trimeth- oprim and the aldehyde triethyl orthoformate in 1:1 M ratio. The metal complexes of Cu^{2+} , Zn^{2+} and La^{3+} were derived from the ligand I. Based on the elemental analysis and the IR, UV–Vis, ¹ H NMR and MS spectra analyses the chemical structures were emphasized. The γ -irradiation stability of the products was investigated via the post-radiation spectral analysis by means of UV–Vis techniques. Some radiolysis products were suggested with the guidance of the MS results. Also, the thermal stability of the Zn-complex was examined by the thermogravimetric analysis (TGA) which confirmed the establishment of coordination. Relatively low molar conductance values were observed for the Cu- and Zn-complexes sug-
	gesting the association of the anions in the coordination sphere and consequently the non-elec- trolytic behavior. The ionic structure of the La-complex was inferred to obey the ratio 1:2
	electrolyte.
	The magnetic properties together with the UV-Vis reposted data revealed the octahedral coordination of the Zn- and La-complex and the tetragonal distortion geometry of the Cu-com-
	plex. The La-complexes revealed only moderate inhibition against the Gram-negative <i>Escherichia coli</i> , whereas the Zn-complex revealed significant inhibition. The latter showed also similar effect against the Gram-positive <i>Bacillus subtilis</i> and <i>Streptococcus pyogens</i> (ATCC-19615)
	© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

* Corresponding author.

E-mail address: raoufokasha@yahoo.co.uk (R.O. Aly). Peer review under responsibility of King Saud University.



1. Introduction

Various heterocycles occupy an important place owing to their versatile bioactivities due to the presence of multifunctional groups (Joseyphus et al., 2006). Schiff-bases and pyridine

http://dx.doi.org/10.1016/j.arabjc.2011.09.017

1878-5352 © 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

derivatives are reported to possess significant antibacterial, antifungal and anticancer activities. The mode of action may involve the formation of a hydrogen bond through the azomethine nitrogen atom with the active centers of cell constituents, resulting in interference with the normal cell processes (Venugaopala and Jayashree, 2003; Vashi and Naik, 2004; Chohan et al., 2004).

In addition to the nitrogen atom, Schiff-base possess at least one functional group so situated that, on complexation with a metal ion, five- or six-membered ring is formed. Metal chelates derived from Schiff-bases have been well known for over one hundred years. A wide variety of chelating Schiff-bases can be made by changing the nature and position of the functional group and introducing different substituents into the reacting molecules (Sunatsuki et al., 2002; Che and Huang, 2003; Khanmohammadi et al., 2007; Di Bernardo et al., 2007; Ruck and Jacobsen, 2002; Adsule et al., 2006; De Geest et al., 2007; Beckmann and Brooker, 2003; Brooker, 2001).

It was reported that incorporation of the transition metal into Schiff-bases augment the biological activity of the ligand and decreases the cytotoxic effects of both the metal ion and ligand on the host. The increase in activity of metal chelates with the increase in their concentration is due to the effect of metal ions on the normal cell processes (Raman et al., 2001). In the past few decades the Schiff-base complexes are becoming increasingly important as biochemical, analytical and antimicrobial reagents (Tümer et al., 1998; Pyrz et al., 1985). Hassan et al. (1997) reported that 6-amino-5-cyano-1,4-dihydro-4-pmethoxyphenyl-1,3-diphenyl pyrano [2,3-c] pyrazole reacts with triethyl orthoformate in acetic anhydride to give ethyl N-(5-cyano-1,4-dihydro-4-p-methoxyphenyl-1,3-diphenyl-pyrano [2,3-c] pyrazole-6-yl) methanimidate. Metal complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with salicylidine-2-aminobenzimidazole were synthesized (Kriza et al., 2000). It was proved that the ligand is coordinated to the metal ions in a tetradentate manner with O, N, and N donor sites of the phenolic-OH, azomethine-N and benzimidazole-N₃.

In the present work the Schiff-base ethyl N-2-amino-5-(3,4,5-trimethoxybenzyl) pyrimidine-4-ylformimidate was prepared by the condensation reaction between trimethoprim and triethyl orthoformate. Some ligand metal-complexes were synthesized and characterized by physicochemical and spectral analyses. Some title compounds were subjected to γ -radiation and the aftermath was spectrally investigated.

2. Experimental

2.1. Materials

All the employed chemicals were Merck-Germany, products. The Schiff-base implemented amine is trimethoprim and the applied aldehyde is triethyl orthoformate. Metal-complexes were prepared by using the metal salts: Cu(CH₃COO)₂·H₂O, Zn(CH₃COO)₂·4H₂O and LaCl₃·7H₂O. Solvents and other used chemicals were of highly pure grade.

2.2. Instruments

The IR spectra were recorded by Perkin Elmer 57928 RXIFT-IR systems. Electronic absorption measurements were performed by Perkin Elmer lambda 35 UV–Vis spectrophotome ter. The ¹H NMR spectra were carried out by Varian, Gemini 200 MHz spectrometer. Hewlett Packard MS 5988 spectrometer was used for mass spectrometry. Thermal analysis was applied by Shimadzu 50. Gamma-cell 220A was used for irradiation processes. Conductance Engineered System, USA, was employed for the conductometric titration and molar conductance measurements.

2.3. Methods

The investigation was supported by the conductometric titration by titrating 10 ml of 10^{-3} M metal ion solution with increasing volume of 10^{-3} M complexing agent solution of Schiff-base using dimethyl sulfoxide (DMSO) as the solvent and the conductance was then recorded after stirring for about 2 min and correction for dilution. The least square regression (Chalt and Waston, 1962) was applied and the following equation was implemented:

Y = mX + b

where Y is the conductance volume, X is the volume of solution, m is the slope and b is the intercept. The yields of both methods admitted the least ratio of 1:1. The molar ratio investigation was carried out by preparing 1.5 ml metal salt solutions kept constant at 10^{-3} M in dimethyl formamide (DMF) while adding the ligand at a regular variable concentration of $0.4-4 \times 10^{-3}$ M. The UV absorbance of the mixed

Compd. no.	Product								
	Color	M.P. (°C)	Yield/g (%)	M.F.	Elemental analysis calcd./found				
					C (%)	H (%)	N (%)	M (%)	
I	Yellow	292–294	5.5 (79)	$C_{17}H_{22}N_4O_4$	58.9 55.3	6.40 6.10	16.17 16.19	-	
Ia	Green	225–227	1.5 (68.68)	$C_{19}H_{28}N_4O_8Cu$	45.28 44.36	5.60 5.43	11.12 9.95	12.61 11.91	
I _b	White	223–225	1.4 (69.30)	$C_{19}H_{28}N_4O_8Zn$	45.11 45.06	5.58 5.35	11.08 11.01	12.93 12.97	
I _c	White	219–221	1.8 (78.53)	$C_{17}H_{25}Cl_2N_4O_6La$	34.54 34.61	4.26 4.19	9.48 9.21	23.49 23.15	

The Schiff-base (I) was prepared by condensation reaction in which the aldehyde, 0.1 mol, was dropwise added to the amine, 0.1 mol, with continuous stirring. Thereafter, the reaction mixture was heated at 100 °C for about 10 min in the presence of 5 ml ethanol or acetic acid. The isolated yields were purified by recrystallization from a solvent (Table 1).

Metal complexes were prepared by the addition of equimolar metal salt solution, 0.004 mol, to the Schiff-base in 25 ml ethanol. Thereafter, the reaction mixture was heated under reflux for 6 h. The solvent was then allowed to evaporate at room temperature (Table 1).

A complementary study based on the electronic absorption spectra and the magnetic moment measurement of metalcomplex, via Faraday method, was employed to envisage the coordination geometry. The UV–Vis absorption within, 200–1100 nm, was examined for DMF 10^{-5} M solutions in the UV- and 10^{-3} M in the Visible sector at room temperature. Meanwhile, the molar conductance of metal-complexes was detected in 10^{-3} M DMF solutions at room temperature.

Irradiation process was carried out for 10^{-5} M in the UV- sector and 10^{-3} M in the Visible-sector DMF solutions of the selected synthesized substances by an integral gamma dose of 30 kGy at a dose rate of 1.2 Gy s⁻¹ under ambient conditions. The post-radiation aftermath was followed up by UV–Vis spectral analysis at the above-mentioned concentrations. The synthesized compounds were also tested for the antimicrobial activity using ampicillin as a reference (Hewitt and Vincent, 1989).

3. Results and discussion

3.1. Schiff-base structure analysis

Based on the means of elemental analysis and the reported data of the IR, UV, NMR and MS measurements, the configuration of Schiff-base I was reasonably suggested.

3.2. IR

Two weak bands at 3330 and 3174 cm⁻¹ were characterized for the amines group's bonds. The aromatic C–H bond was demonstrated by the stretching vibration at 3093 cm⁻¹, whereas the bands at 2938 and 2840 cm⁻¹ were assigned for the aliphatic C–H bonds of the azomethine group. Meanwhile, the bonds at 1646 and 1586 cm⁻¹ were predicated for the C=N bonds in the azomethine and the pyrimidine rings, respectively. The sharp bond 1502 cm⁻¹ was ascribed to C=C bonds and the bonds at 1414 cm⁻¹ were accounted for the aromatic C–H deformation mode of vibration. Meanwhile, the band which appeared at 1306 cm⁻¹ was determined for the C–N bonds. The C–O–C bonds were suggested to appear by the bands at 1240, 1122 and 1004 cm⁻¹.

3.3. UV

Within the region $\lambda_{\text{max}} = 202-247$ nm unresolved structures appeared suggesting the (${}^{1}L_{a} \leftarrow {}^{1}A$) transition of the phenyl ring, whereas the peak at $\lambda_{\text{max}} = 259$ nm was accounted for the (${}^{1}L_{b} \leftarrow {}^{1}A$) phenyl ring transition. The $\pi - \pi^{*}$ transition of



Scheme 1 Ethyl N-2-amino-5-(3,4,5-trimethoxybenzyl) pyrimidine-4-ylformimidate.

the C=N group was presented by the absorption at $\lambda_{max} = 272$ nm, while the broad bands at $\lambda_{max} = 330$ nm were ascribed to the n- π^* transition of the azomethine group.

3.4. ¹H NMR

The Schiff-base I in DMSO-d₆ revealed the following ¹HNMR signals. A triplet at δ 1.3 represents the methyl protons in the ethyl group, whereas the methylene proton could be detected as a quarter at δ 3.72. Meanwhile, the protons of the methylene group connecting the phenyl and pyrimidine rings could be assigned by the singlet at δ 3.57. The chemical shift at δ 3.6 was attributed to the methoxy group protons. The amine group connected to the pyrimidine ring exhibited a singlet at δ 4.4 which disappeared by the addition of D₂O. The aromatic protons in the substituted aromatic ring with the methoxy groups demonstrated two signals at δ 7.5 and δ 7.8. Further, the aromatic protons of the mono substituted phenyl revealed a multiplet within the region δ 6.4–6.8. The azomethine proton exhibited a singlet at δ 8.25, whereas the pyrimidine ring proton gives a singlet at δ 8.35.

3.5. MS

The mass spectrum of the Schiff-base I displayed the molecular peak at m/e = 346 (31.7%). The ion peak at m/e = 318 (100%) was assigned for the base M^+ ($C_{15}H_{18}N_4O_4$), whereas, m/e = 290 (89.7%) for M^+ ($C_{14}H_{18}N_4O_3$), m/e = 275 (87.6%) for M^+ ($C_{14}H_{17}N_3O_3$), m/e = 259 (57.9%), for M^+ ($C_{14}H_{15}N_2O_3$), m/e = 243 (72.4%) for M^+ ($C_{13}H_{13}N_3O_2$), m/e = 228 (57.9%) for M^+ ($C_{13}H_{12}N_2O_2$), m/e = 200 (30.3%) for M^+ ($C_{11}H_{12}N_4$), m/e = 123 (35.2%) for M^+ ($C_5H_7N_4$), m/e = 106 (14.5%) for M^+ ($C_5H_4N_3$) and m/e = 77 (30.3%) for M^+ (C_6H_5). The elemental and spectral analyses may suggest the following structure for I represented in Scheme 1.

3.6. Metal-complexes analyses

The metal-complexes of the Schiff-base I_{a-c} were synthesized by incorporating the metal ions Cu^{2+} , Zn^{2+} and La^{3+} , respec-

Table	2	The	magnetic	properties	of	the	metal	Schiff-base
comple	exes							

Complex	$\mu_{\rm eff}$ (B.M.)	
No.	Metal	
Ia	Cu	1.85
I _b	Zn	Diamagnetic
Ic	La	Diamagnetic

tively. Illustration of the metal-complex configuration was undergone by applying the elemental, Table 2, and spectral analyses.

3.7. IR

The associated water molecules were detected in $I_{a,c}$ by the bands observed at 3552 and 3474 cm⁻¹, respectively. The aromatic C–H bond was located at 3254, 3067 and 3172 cm⁻¹ in I_{a-c} , respectively, while, the in-plane bending deformation of the bond appeared at 1434, 1450 and 1422 cm⁻¹, respectively. Weak bands were observed at 2970, 2970 and 2918 cm⁻¹ in the same spectra, respectively, representing the aliphatic C–H bands of the azomethine and the acetate groups. Meanwhile, the bands observed at 1570, 1502 and 1658 cm⁻¹ in I a-c, respectively, were assigned also to the azomethine group.

The acetato complexes displayed $v_{as} \text{COO}^-$ and $v_{sym} \text{COO}^$ at 1640 and 1545 cm⁻¹ and 1348 and 1363 cm⁻¹ in the spectra of Cu- and Zn-complexes, respectively. Also, the C–O–C bonds revealed the bands at 1238, 1205 and 1238 cm⁻¹ in I_{a-c} spectra, respectively. Meanwhile, the bands at 620, 620 and 626 cm⁻¹ in the same complexes, respectively, were assigned for the M \leftarrow N bond. In addition, the M \leftarrow O bands were also predicated by the bands observed at 452, 379 and 512 cm⁻¹, respectively. In addition, the bands at 3452 and 3330 cm⁻¹ in Cu- and La-complexes were attributed to the N–H bonds.

3.8. UV–Vis and magnetic behavior: coordination geometry

The magnetic properties of metal-complexes, as a result of the isolating effect of the ligand yield direct information on electronic configuration of the central ions, oxidation state of metal ion and the number of the unpaired electrons of the d-shell.

Metal-complexes $\mathbf{I_a}$, $\mathbf{I_b}$ and $\mathbf{I_c}$ displayed absorption bonds within $\lambda_{\text{max}} = 203-246$ nm and $\lambda_{\text{max}} = 250-255$ nm that reveal the transitions of the ligand phenyl ring (${}^{1}\mathbf{L_a} \leftarrow {}^{1}\mathbf{A}$) and (${}^{1}\mathbf{L_b} \leftarrow {}^{1}\mathbf{A}$). On the other hand, the bonds within $\lambda_{\text{max}} = 272-$ 274 nm represented the $\pi - \pi^*$ transitions, whereas the $n - \pi^*$ transitions of the C=N in the azomethine groups appeared within $\lambda_{\text{max}} = 330-331$ nm. The d–d transitions were detected within $\lambda_{\text{max}} = 379-797$ nm.

The measured magnetic moment at room temperature of Cu, $\mu_{\rm eff} = 1.85$ B.M., is consistent with the normally observed for distorted octahedral for Cu(II)-complexes (Kumar et al., 1991). The ${}^{2}\text{E}_{g}$ and ${}^{2}\text{T}_{2g}$ states of the octahedral Cu²⁺ ion (d⁹, ${}^{2}\text{D}$ term) split under the influence of the tetragonal distortion due to ligand field and Jan-Teller distortion effect (Miessler and Tarr, 2004). The electronic spectrum of I_a exhibited absorption bands within $\lambda_{max} = 379-797$ nm which can be assignable to the expected spin allowed transition produced by the distortion effect: ${}^{2}\text{B}_{1g} \rightarrow {}^{2}\text{A}_{1g}$, ${}^{2}\text{B}_{1g} \rightarrow {}^{2}\text{B}_{2g}$ and ${}^{2}\text{B}_{1g} \rightarrow {}^{2}\text{E}_{g}$. The Zn- and La-complexes I_b and I_c are diamagnetic possessing



Scheme 2 Analyses conformations suggested for the metal-complexes I_a , I_b and I_c .

the octahedral coordination. Measured magnetic moments are tabulated in Table 2.

3.9. ¹H NMR spectra

¹H NMR spectrum of Zn-complex I_b was recorded in DMSO-d₆. The azomethine proton showed a singlet shifted at δ 8.2. Meanwhile, the aromatic protons exhibited multiplet signals within δ 6.5–7.3. The presence of a number of methyl groups yielded a high-intensity shift at δ 2. In addition, the disappearance of the amine proton shift suggests the participation of the amine group in the complexation process.

In view of the aforementioned analyses the conformations may be suggested for the metal-complexes I_a , I_b and I_c represented in Scheme 2.

4. Miscellaneous behaviors

4.1. γ-Irradiation stability

In 10^{-5} M DMF solution ligand I was γ -irradiated at conditions of: 30 kGy total integral dose at a dose rate of 1.2 Gy s⁻¹, neutral medium and ambient air and room temperature. At relatively low dose rate the linear energy transfer favors the non-inter radical reactions (Baxendale and Wardman, 1975), and the excitation energy received by the aromatic systems is channeled to relatively low-energy triplet excited states which have a low probability of dissociation (Burns and Barker, 1968). Heterocyclic compounds that have aromatic character are also resistant toward radiation if the yield of H₂ is taken as the criterion, although they may produce appreciable yields of polymer (Berk and Gisser, 1973). The reason is that aromatic radicals generally combine rather than disproportionate (Proskurnin et al., 1956).

As ligand I possesses two different types of aromatic rings, one of them is heterocyclic, it also possesses two different alkyl-oxygen groups, namely $-O-CH_3$ and $-O-C_2H_5$. The radiolysis of ethers tends to center on the oxygen functional group rather than on the hydrocarbon chain. In other words, band scission is predominantly C–O and C–C, that is adjacent to the ether oxygen, rather than the C–H scission (Sumiyoshi et al., 1985). The hydrocarbons formed in greatest yields by radiolysis result from the rupture of the alkyl-oxygen bond (Kiss and Teply, 1971).

With an analogy to γ -radiolysis of acetone at a relatively low dose rate, DMF methyl radicals may produce similar products, e.g. H₂, H₄ and CO, and also attack the substrate yielding several products (Grimsrud and Kebrle, 1973).

Generally, the impact of γ -radiation on the UV spectrum of I was significant as the phenylic transition region, within



Scheme 3 Postulated radiation-induced species.

 $\lambda_{\text{max}} = 200-260$ nm, exhibited various better resolved shapes. Contrarily, the next region, within $\lambda_{\text{max}} = 260-320$ nm, revealed the destruction of the $n-\pi^*$ transition at $\lambda_{\text{max}} = 320$ nm of the azomethine bond and the cluster of the $\pi-\pi^*$ transitions into an indistinctive shape of markedly higher absorbance. It is evident that γ -irradiation generated differentiable structures with appreciable formation of longer conjugated systems borne by radical-radical recombination, beside the rupture of the C=N band. Guided by the MS yields, as a first approach (Dessouki et al., 1986), three potential radiolysis products may be suggested shown in Scheme 3:

The metal-complex I_a demonstrated within the region, $\lambda_{max} = 200-280$ nm, showed a remarkably higher absorbance steady character all over the spectral region. Meanwhile, within the range $\lambda_{max} = 290-340$ nm nearly five distinctive shapes instead of ambiguous fingerprint were detected with substantial reduction in absorbance. On the other hand, over the extended visible region, at a concentration of 10^{-3} M, a slightly resolved hump within the range $\lambda_{max} = 650-850$ nm was turned out to a smooth hump with a $\lambda_{max} = 711$ nm. Evidently, distortion of the complex structure by irradiation is definite at the applied conditions with consequent formation of several structures shown by multi resolved fine spectral shapes (Becker, 1997).

4.2. Thermal stability

The thermogram of the Zn(II) metal-complex I_b revealed four decay stages. The first showed a loss of 9% at 235 °C describing the missing of [C₂H₅O] adduct. The followed stage was of 17.86% which took place within the region 235–320 °C corresponding to the isolation of one acetate group and the adduct [CH₃O]. The third decay was of 25.95% within the range 320–590 °C of the adduct [C₆H₄N₄]. The last loss was of 29.3% within the range 590–910 °C attributed to the separation of the adduct [C₉H₁₀O₂]. A residue of 18.1% corresponding to 98 mass unit was thermally stable up to 1000 °C and was referred to ZnO and half oxygen molecules.

4.3. Molar conductance

The molar conductance of the metal-complexes I_{a-c} was measured in 10^{-3} M DMF solution at room temperature. The respective results of Cu-, Zn- and La-complexes were 12.6, 19.8 and 412 Ω^{-1} cm² mol⁻¹. The relatively low values of $I_{a,b}$ suggest that the anions associated with the metal-complexes are neutral and behave as non-electrolyte complexes. The reported values indicate the 1:2 electrolyte in the case of I_c suggesting the ionic nature (Ying et al., 2004).

4.4. Antimicrobial activity

The metal-complexes I_{a-c} were investigated with reference to Ampicillin while dissolved by 1 g/ml DMSO. Against the Gram-positive *Bacillus subtilis* (NCTC-1040), only I_a showed moderate inhibition. Further, against *Streptococcus pyogens* (ATCC-19615), similar results were obtained.

The Gram-negative bacteria examinations exhibited the following: for *Escherichia coli*, I_a showed very high activity, whereas I_b and I_c revealed significant and moderate inhibition, respectively. For clostridium, only I_a showed moderate inhibi-

tion using Clofran as a reference negative antifungal results were obtained out of all applied metal-complexes.

5. Conclusion

The chemical structure of the Schiff-base I and metalcomplexes derivatives I_{a-c} was discussed and verified on the basis of elemental and spectral analyses. The coordination process was confirmed by the discrepancies and the appearance of new signals in the different types of spectra. The Cu-complex revealed the tetragonal distortion effect, whereas the Zn- and La-complexes demonstrated the octahedral coordination. The γ -irradiation process at the applied conditions revealed for I_{a-c} obvious less stability in comparison with the ligand as detected by the post-radiation trace within the UV-Vis spectral region. The radiolysis of the ligand and metalcomplex substrates as well as the solvent was argued and some likely produced species were suggested. The TGA of $I_{\rm b}$ confirmed the coordination process with the inclusiveness of the acetate group and the remainder of ZnO. The relatively low molar conductance values shown for Ia,b suggest that the anions associated with the metal-complexes are involved in the coordination sphere. Thus, the metal-complexes are neutral and behave as non-electrolyte complexes. The ionic structure of I_c was inferred by the ratio 1:2 electrolyte. On the other hand, Ic revealed only moderate inhibition against the Gramnegative bacteria *E. coli*, whereas I_{b} gave significant inhibition. The latter showed similar effect against the Gram-positive B. subtilis and S. pyogens (ATCC-19615).

References

- Adsule, S., Barve, V., Chen, D., Ahmed, F., Dou, Q.P., Padhye, S., Sarkar, F.H., 2006. J. Med. Chem. 49, 7242.
- Baxendale, J.H., Wardman, P., 1975. US Dept. Commerce National Bureau of Standards, Washington, DC.
- Becker, G., 1997. Anal. Chim. Acta 340, 181-189.
- Beckmann, U., Brooker, S., 2003. Chem. Rev. 222, 17.
- Berk, S., Gisser, H., 1973. Radiat. Res. 56, 71.
- Brooker, S., 2001. Coord. Chem. Rev. 222, 33.
- Burns, W.G., Barker, R., 1968. In: Gaumann, T., Hoigne, J. (Eds.), Aspects of Hydrocarbon Radiolysis. Academic, NY (ch. 2).

Chalt, J., Waston, H.R., 1962. J. Chem. Soc. 2, 545.

- Che, Chi-Ming, Huang, Jie-Sheng, 2003. Coord. Chem. Rev. 242, 27.
- Chohan, Z.H., Pervez, H., Rauf, A., Khan, K.M., Supuran, C.T., 2004. J. Enzym. Inhib. Med. Chem. 19, 417.
- De Geest, D.J., Noble, A., Moubaraki, B., Murray, K.S., Larsen, D.S., Brooker, S., 2007. Dalton Trans., 467.
- Dessouki, A.M., El-Assy, N.B., Aly, R.O., Ibrahim, E.H.M., El-Dossouky, M.M., 1986. J. Rad. Nucl. Chem. 100 (1), 49.
- Di Bernardo, P., Zanonato, P.L., Tamburini, S., Vigato, P.A., 2007. Inorg. Chim. Acta 360, 1083.
- Grimsrud, E.P., Kebrle, P., 1973. J. Am. Chem. Soc. 95, 7939.
- Hassan, S.M., Khafagy, M.M., Emam, H.A., El-Maghraby, A.A., 1997. J. Indian Chem. Soc. 74, 27–29.
- Hewitt, W., Vincent, S., 1989. Theory and Application of Microbiological Array. Academic Press Inc., New York.
- Joseyphus, R.S., Dharmaraj, C.J., Nair, M.S., 2006. Trans. Met. Chem. 31, 699.
- Khanmohammadi, H., Amani, S., Lang, H., Rüeffer, T., 2007. Inorg. Chim. Acta 360, 579.
- Kiss, F., Teply, J., 1971. Int. J. Radiat. Phys. Chem. 3, 503.
- Kriza, A., Reiss, A., Florea, S., Caproiu, T., 2000. J. Indian Chem. Soc. 77, 207.
- Kumar, N.R.S., Nethiji, M., Patil, K.C., 1991. Polyhedron 10, 365.
- Miessler, G.L., Tarr, D.A., 2004. Inorganic Chemistry, third ed. Pearson–Prentice Hall.
- Proskurnin, M.A., Barelko, E.V., 1956. In: Proc. Int. Conf. Peaceful Uses Atomic Energy, vol. 7. United Nations, NY, p. 538.
- Pyrz, J.W., Roe, A.I., Stern, L.J., Que, J.R., 1985. J. Am. Chem. Soc. 107, 614.
- Raman, N., Raja, Y.P., Kulandaisamy, A., 2001. Proc. Indian Acad. Sci. (Chem. Sci.) 113, 183.
- Ruck, R.T., Jacobsen, E.N., 2002. J. Am. Chem. Soc. 124, 2882.
- Sumiyoshi, T., Tsugaru, K., Yamdada, T., Katayama, M., 1985. Bull. Chem. Soc. Jpn. 58, 3073.
- Sunatsuki, Y., Motoda, Y., Matsumoto, N., 2002. Coord. Chem. Rev. 226, 199.
- Tümer, M., Erdoğan, B., Köksal, H., Serin, S., Nutku, M.Y., 1998. Synth. React. Inorg. Met. Org. Chem. 28, 529.
- Vashi, K., Naik, H.B., 2004. Eur. J. Chem. 1, 272.
- Venugaopala, K.N., Jayashree, B.S., 2003. Indian J. Heterocycl. Chem. 12, 307.
- Ying, L.M., Zhi, H.P., Cheng, Z.J., Yi, L., Xi, X.K., 2004. Chin. J. Chem. 22, 162.