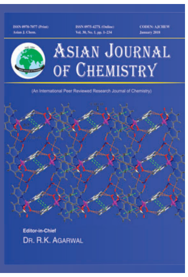
Asian Journal of Chemistry; Vol. 30, No. 8 (2018), 1863-1867

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2018.21353



Synthesis, Stereochemical and Biological Studies of Mono-nitrophenol Complexes with Benzofurathiosemicarbazide Ligand

MUKTI VERMA[1], MONI VERMA[2], SUMAN RANI[2] and NAZIA TARANNUM[1,*]

[1]Department of Chemistry, Chaudhary Charan Singh University, Meerut-250 005, India
[2]Department of Chemistry, Nanak Chand Anglo Sanskrit College, Meerut-250 003, India

*Corresponding author: E-mail: naz1012@gmail.com

Received: 27 March 2018; *Accepted*: 16 May 2018; *Published online*: 30 June 2018; AJC-18987

The present work deals with the preparation and characterization of complexes of benzofuron-2-carboxy-phenyl thiosemicarbazide and benzofuro-2-carboxy-[4'-chlorophenyl]thiosemicarbazide with Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) mono-nitrophenates. The structure of newly synthesized metal complexes and the ligands were established with UV-visible spectroscopy, infrared spectroscopy and magnetic studies. The ligand and the metal complexes were also screened and evaluated for their fungicidal activity against different fungi using growth method.

Keywords: Benzofurathio-semicabazide, Magnetic moment, Antifungal activity, Stereochemical, Biological activity.

INTRODUCTION

Domagk [1] observed tuberculostic activity of thiosemicarbazone and their related compounds. Thiosemicarbazide and their derivatives have shown various biological activities [2-5] and they are used in medicine, especially in the cure of tuberculosis. Antimicrobial and antitumor activity have also been shown by some thiosemicarbazones [6,7]. Thiosemicarbazones in animal system has also been noted [8-10]. Thiosemicarbazone has shown activity against viruses, protozoa and smallpox [11,12]. Thiosemicarbazones and their derivatives are also active against influenza, pesticides and fungicides because of their ability to form chelates with traces metals [13-16]. In recent years, thiosemicarbazones have been analyzed for analytical determination of metals [17]. Recently, few researchers [18,19] have reported the chelation and electronic properties of aromatic and aliphatic semicarbazones obtained by organic moieties with biological interest. The complexing property of oxygen-nitrogen, sulphur-nitrogen and oxygen-nitrogen-sulphur donor ligands [20,21] and their biological activity has also been reported. It is well known fact that the drug increases the activity when used in the form of metal complexes. A number of metal chelates inhibit tumor growth. In the treatment of cancer, the active species is not the thiosemicarbazone but its metal chelate. The study of different models of transition metal complexes for understanding many biochemical processes is very interesting [22,23].

Metal complexes [24,25] play a fundamental role in metabolic and toxicological functions in the biological systems. Amongst the metal complexes, cobalt complexes have shown importance because of their unique property of functioning as oxygen carriers [26,27]. It is a well known fact that the biological activity of a compound depends upon its coordinating ability [28]. Transition metals and their derivatives have evoked much interest due to their inherent bio-potency [29,30], striking structural aspects and unique stereo- and magneto-chemistry [31]. Biligand coordination compounds are estimated to offer valuable information on magnetic properties, electronic spectra, flexidentate behaviour of polydentate ligands and stereochemistry. However, the literature survey revealed that except a few scattered references [21,32,33] no systematic work have been reported on the complexes of thiosemicarbazide ligand containing 2-substituted benzofuran hydrazide moiety. So it is worthwhile to prepare transition metal complexes of thiosemicarbazide ligand containing 2-substituted benzofuran hydrazide moiety and study their structural and biological activity.

The present work deals with the preparation and characterization of complexes of benzofuron-2-carboxy-phenyl thiosemicarbazide and benzofuro-2-carboxy-[4'-chlorophenyl]thiosemicarbazide with Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) mono-nitrophenates. The synthesized complexes were characterized by IR, UV-visible and magnetic studies. Ligand and their metal complexes were also screened for their antifungal activity against different fungi using growth method at different concentrations. The stereochemical properties of the complexes were also analyzed.

EXPERIMENTAL

All chemicals used were of analytical grade otherwise purified before use. Metal salts of Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) were procured from Fischer Scientific, India. The solvents were dried and distilled before use following the standard procedures.

Metal contents and sulphur were determined by using standard methods. C, H and N were determined at CDRI Lucknow, India. The magnetic susceptibility of the complexes were made on Gouy's balance using $Hg[Co(NCS)_4]$ as calibrant at room temperature. The IR spectra were recorded from IIT Roorkee, India. The electronic spectra of complexes were recorded on Elico CL-24 spectrophotometer. All the complexes gave satisfactory analysis of metal nitrogen and sulphur.

Preparation of ligand: The ligand benzofuro-2-carboxyphenyl thiosemicarbazide and benzofuro-2-carboxy-[4'-chlorophenyl]thiosemicarbazide were prepared in two steps. In the first step, benzofuran-2-carboxy hydrazide was prepared by method reported in literature [16]. In the second step, 1 mol of phenyl isothiocyanate/*p*-chlorophenyl isothiocyanate was added to ethanolic solution of 1 mol of benzofuran-2-carboxyhydrazide with constant stirring (Fig. 1). The reaction mixture was refluxed on water bath for about 8 h. On completion of reaction, the solid product was filtered washed with alcohol and recrystallized from alcohol and dried in vacuum.

Preparation of complexes: Metal mono-nitrophenates were prepared by adding metal carbonate to hot aqueous solution of mono-nitrophenol till effervescence ceases. A little excess of metal carbonate was added. The whole reaction mixture was heated on water bath and filtered. The filtrate on concentration gives crystals of metal nitrophenates. Metal complexes were prepared by adding 0.2 mol of metal-mono-nitrophenates to 0.2 mol of ligand in alcohol (Fig. 2). The reaction mixture was refluxed on water bath for about 6 h. The solution was concentrated and cooled. The crystalline, coloured complexes were filtered, washed with alcohol and dried in vacuum. Analytical data for the complexes indicates 1:2 stoichiometry for all the metal complexes. All the metal complexes showed high melting point and are stable in air. The complexes were insoluble in common solvents.

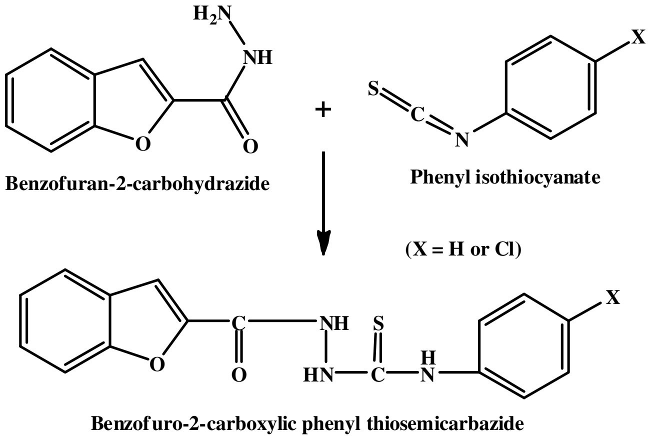


Fig. 1. Preparation of thiosemicarbazide ligands

Antifungal activity: The fungicidal activity of ligands as well as their metal complex was determined using the growth method. The activity was determined against various fungi *i.e. Drechslera tetramera, Fusarium-oxysporum* and *Aternaria alternata* at different concentrations. The testing samples were incorporated in warm Czapeck's Dox agar medium so as to give different concentration *viz.* 100, 200 and 500 ppm. The test samples and the medium were autoclaved at 15 lbs for 15 min and then shaken well to give uniform dispersal of the chemical. The samples were poured into sterilized petri-dishes keeping three replications of each treatments and a check without chemicals. Then the plates were inoculated centrally

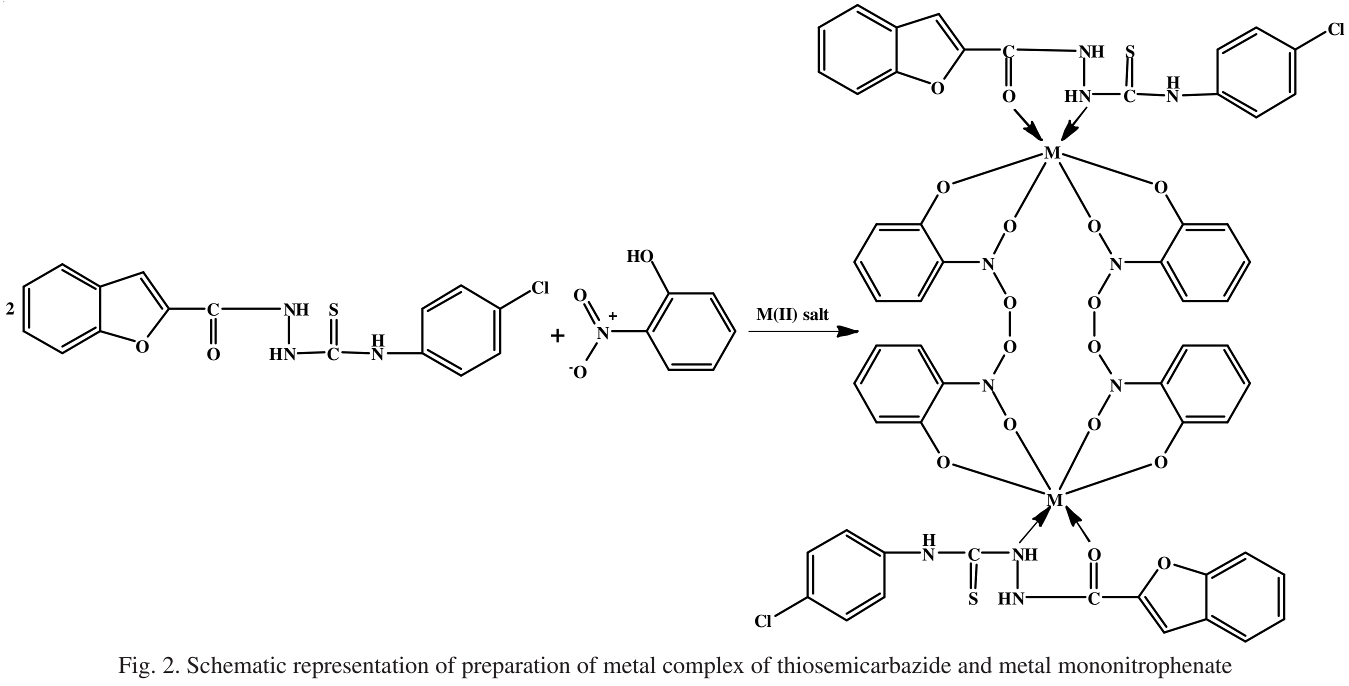


Fig. 2. Schematic representation of preparation of metal complex of thiosemicarbazide and metal mononitrophenate

with a mycelia disc from 7 days old culture of the fungi towards complex.

RESULTS AND DISCUSSION

Infrared spectra: The thiosemicarbazide ligands exhibit three bands in the region 3441-3400, 3365-3277 and 3130-3072 cm^{-1} assigned to $\nu(^4NH)$, $\nu(^2NH)$ and $\nu(^1NH)$, respectively [34,35]. In the spectra of the metal complexes, the bands due to $\nu(^4NH)$ shift to higher wave number by about 10-20 cm^{-1} and in some complexes it remains unaltered indicating non-involvement of nitrogen of $\nu(^4NH)$ group in coordination with metal ions. The band due to $\nu(^2NH)$ shift to lower wavenumber side by about 20-30 cm^{-1} in all the complex. The bands observed in the region 3130-3072 cm^{-1} remain practically unaltered or shift slightly to higher side indicating no coordination.

The weak bands observed in the regions 2810-2780 cm^{-1} are assigned to stretching vibrations of intra-molecular hydrogen bonding between ν(CO) and $\nu(^2NH)$ group [36]. The absence of any band above 3500 cm^{-1} due to ν(OH) and 2600-2500 cm^{-1} due to ν(SH) suggest that ligands exists in thioketo form. The strong band observed [37] at 1659 and 1675 cm^{-1} in free ligands are assigned to ν(CO) vibrations. These bands shift to lower wave number by about 30-50 cm^{-1} in all the metal complexes. This suggests the coordination of oxygen with metal ions. The positive shift of ν(N-N) bands observed at 1010 and 1020 cm^{-1} in free ligands are shifted to higher wavenumber by 10-15 cm^{-1} in the complexes thereby showing the coordination of one of the nitrogen atoms of hydrazine moiety in bonding [38]. The thio-keto ν(C=S) band observed in the region 37-720 cm^{-1} shows no shift in the metal complexes compared with free ligands. This shows sulphur atom of (C=S) has not taken part in coordination. The thio-amide [39] bands observed in the regions 1540-1520, 1360-1340, 1080-1050 and 740-700 cm^{-1} due to amide, remain unaltered or do not show considerable change in the complexes suggesting the non-involvement of (C=S) group in bonding with metal ions.

Manganese(II) complexes: Mn(II) ion in a weak octahedral field shows paramagnetism corresponding to five unpaired electrons having magnetic moment value 5.92 B.M. with the ground state $(t_{2g})^3$ $(eg)^2$ while in the strong ligand field it assumes $(t_{2g})^5$ configuration. The strong field ligand would force two of the spin pairs leaving only one unpaired electron, hence such compounds exhibit magnetic moment μ_{eff} 2.5 B.M., a little larger than the spin only value for one unpaired electron. Since Mn(II) ion has d^5 configuration, it is capable of forming spin free as well as spin paired complexes. Due to additional stability of half filled '*d*' shell, spin free complexes are most predominant since spin free Mn(II) complexes have an orbitally non-degenerate 6*s* ground level spin only. The magnetic moments of 5.92 B.M. is however, expected will be independent of temperature and stereochemistry. In the present study, these complexes show magnetic moment 5.85 B.M. suggesting thereby that it is spin free octahedral complex with five unpaired electrons. The absorption bands in the spectra correspond to the spin forbidden transition from the ground state $^6A_1$, to the levels arising from 4E, 4P and 4D excited state of the free ion. Further, three absorption bands due to transition to the levels arising from 4F state will occur in the ultraviolet region. The energies of $^6A_1$, 4E(4D) and 4E(G), 4A(4G) states are independent of 10 Dq and depends only on B and C. The colour of the Mn(II) complexes studied herein are pale pink. However, the intensity of electronic transition from the ground state to the states of four fold multiplicity is very weak. The complex display three absorption bands at 18680, 22480 and 28300 cm^{-1} assigned to sextet quartet transition.

$$^6A_{1g} \longrightarrow {}^4A_1(4G)\ (\nu_1)$$

$$^6A_{1g} \longrightarrow {}^4E_g(4D)\ (\nu_2) \text{ and}$$

$$^6A_{1g} \longrightarrow {}^4T_{1g}\ (4P)\ (\nu_3) \text{ respectively.}$$

The values of Dq, B (Nephelauxetic ratio) and C have been calculated using the equation suggested by Figgis [40].

Cobalt(II) complexes: The magnetic moment of different types of Co(II) complexes lie in the range 2.1-2.9 B.M. for square planar and 4.2-4.8 B.M. for high spin coordinated complexes. The magnetic moment of cobalt complex was reported to be 4.26 B.M. at room temperature suggesting octahedral geometry. Cobalt(II) ion has $4f(t_{2g})^5$ $(eg)^2$ ground state with the excited state 4p lying 15B higher in energy. In a cubic crystal field, these levels will split into $^4T_{1g}(F)$, $^4T_{2g}$, $^4A_{2g}$ and $^4T_{1g}(P)$ in order of increasing energy. Hence, for octahedral Co(II) complexes three spin allowed bands are expected corresponding to the transitions.

$$^4T_{1g}\ (F) \longrightarrow {}^4T_{2g}\ (\nu_1)$$

$$^4T_{1g}(F) \longrightarrow {}^4A_{2g}\ (\nu_2) \text{ and}$$

$$^4T_{1g}\ (F) \longrightarrow {}^4T_{1g}(P)\ (\nu_3)$$

However, $^4A_{2g}$ state is derived from $(t_{2g})^3$, $(eg)^4$ configuration while the $^4T_{1g}$ (F) state is derived from $(t_{2g})^5$ $(eg)^2$, hence the $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition is a two electron process and will be much weaker than the other transitions. The magnetic and electronic spectra suggest octahedral geometry.

Nickel(II) complexes: Six coordinated Ni(II) ions having $3d^8$ electronic configuration and exhibit a magnetic moment higher than expected for two unpaired electrons in octahedral (2.98-3.22 B.M.) and tetrahedral (3.40-4.21 B.M.). Complexes with square planar geometry are expected to be diamagnetic. This increase in magnetic moment value from that of spin only value has been considered by Nyholm to be due to some mixing of upper state *via* spin-orbit coupling. The paramagnetism observed for present complex is 2.98 B.M. at room temperature which is consistent with octahedral symmetry. In a cubic field, 3F ground state of Ni(II) ion splits into three level, the orbit singlet $^3A_2$ and the orbit triplet $^3T_1$ and $^3T_2$. The first excited term of the free Ni(II) ion 3P transforms as $^3T_{1g}$ under cubic symmetry.

Therefore, three spin allowed transitions have been observed in the present octahedral Ni(II)

$$\{^3A_{2g}\ (F) \longrightarrow {}^3T_{2g}\ (F)\}\ (\nu_1)$$

$$\{^3A_{2g}\ (F) \longrightarrow {}^3T_{1g}\ (F)\}\ (\nu_2) \text{ and}$$

$$\{^3A_{2g}\ (F) \longrightarrow {}^3T_{1g}(P)\}\ (\nu_3)$$

The present complex showed the bands at 8180, 14200 and 23950 cm^{-1} for ν_1, ν_2 and ν_3, respectively which is established for the majority of octahedral Ni(II) complexes while at 8500 cm^{-1} and 15900 cm^{-1} are due to the geometrical distortion and non-identical donor atoms which cause departure from octahedral symmetry. However, the observed spin allowed transition agree well with those predicted by Liehr and Ballhausen energy level diagram for Ni(II) ion in a ligand field of octahedral stereochemistry. The value of B for the complex calculated from ν_1, ν_2 and ν_3 band energies and using the diagonal sum rule. It has been shown that for Ni(II) complexes with an octahedral symmetry, as 10 Dq increases configurational interaction between the high spin $^3T_{1g}(F)$ excited state generally lowers the ratio ν_2/ν_1 from the theoretical value of 1.80 to 1.5-1.72. The value of ν_2/ν_1 for the present complex comes out to be 1.69 B.M. conforming octahedral symmetry for nickel complex.

Copper(II) complexes: The cupric ion has $3d^9$ configuration having one unpaired electron. Its complexes usually have simple square planar to tetragonally distorted octahedral stereochemistry. However, irrespective of the stereochemistry involved, the magnetic moment has been found to be (with spin-orbit coupling constant of 850 cm^{-1}) about 1.90 B.M. Generally, octahedral coordinated Cu(II) complexes have magnetic moment in the range 1.90-2.20 B.M. and the values are independent of temperature. Figgis predicted a magnetic moment > 1.90 B.M. for tetrahedral and < 1.90 BM for square planar and octahedral of Cu(II) complexes. The square planar complexes of Cu(II) ion may rightly be called as extreme cases of tetragonally distorted octahedral geometry around the central metal ion and in such environment the separation between the ground level $^2B_{1g}$ and the components of $^2T_{2g}$ term of Cu(II) ion is larger than in octahedral complexes which possibly seems to be responsible for the lower magnetic moment values of square planar complexes. However, no significant conclusion concerning the stereochemistry of Cu(II) compounds can be drawn nearly on the basis of magnetic data. The electronic spectra of Cu(II) complex show only one broad absorption band at 16000 cm^{-1} which may be assigned to the transition $^3Eg \rightarrow {}^2T_{2g}$ characteristic of distorted octahedral Cu(II) complex. The magnetic moment value of Cu(II) complex is 1.86 B.M. suggesting distorted octahedral stereochemistry.

Zinc(II) complexes: Zn(II) ion shows d^{10} configuration and usually attains tetrahedral geometry using sp^3 hybridization but the possibility of forming penta-coordination (sp^3d) and hexa-coordination (sp^3d^2) cannot be ruled out. Zinc(II) complexes are diamagnetic, since *d-d* transitions are not possible. Their magnetic moment values lie in the range 0.15 to 0.24 B.M. indicating the absence of unpaired electron. In the present case, the value comes to be 0.18 B.M. The magnetic moment values suggest octahedral geometry of Zn(II) complex.

Study of antifungal activity of complexes: The idea that fungi toxicants react mainly with ligands on conidial surface and are primarily accumulated on the surface does not have valid experimental support. However, the migration of fungicides to the sites of action consist a complicated series of reactions that involve both electronic and hydrophobic nature of the toxicants. Since the life processes of organism are controlled and directed by complex and inter related series of enzyme system. However, the metal complexes may penetrate the wall on lipid membrane in the form of simple chelate inhibiting specific enzymes causing toxic reactions among cellular constituent and ultimately causing death of the organism.

The bound metal mostly attacks the functional groups contained in the living tissues. The functional groups most frequently attacks thiol and amino groups. Several amino groups from the amino acids comprise amino pool in the cellular fluids which are particularly the target of pesticides. Certain metal like Cu(II) is also known to exert a striking influence in the sporulation of fungi. However, different fungi seems to differ in their quantities may be cited for its fungicidal effect in majority of the fungi as various Cu-fungicides at higher concentrations.

Role of Mn(II) has been noted in the biosynthesis of some primary and secondary fungal metabolites also. Fe(II) and Mn(II), particularly the former, were observed to be quite effective in altering the potency of fusarie and by preferential chelation in fungus *Fusarium*. It has been shown that chemical control of plant disease are dependent much on heavy metals for its success and in many cases the activity increases after complex formation with an organic radical. The data in colony growth response of *Drechslera tetramera, Aternaria alternate* and *Fusarium oxysporum* at different concentrations of 500, 200 and 100 ppm using three replications in each case are recorded. The analysis of fungicidal result showed a definite pattern existing between fungi toxicity and chemical structure. The result indicates that in untreated control the test fungi grew; on the other hand the growth of fungi is inhibited well by all the complexes. It may be concluded that the ligand posses good fungicidal activity against all the three fungi.

From the fungicidal activity data, it is evident that among all the metal complexes tested for their antifungal activity, Cu(II) complexes are most active fungicides. The fungicidal action of Cu(II) complexes may be explained due to inactivation of enzymes. The other metal complexes are however not much fungi toxic for the particular fungi. Generally, the fungi toxicity enhanced with increase in the dose of complex. However, a correlation between toxicity of metals and their ability to form stable metal chetales revealed the following order.

$$\text{Cu(II)} > \text{Ni(II)} = \text{Co(II)} > \text{Mn(II)}$$

It is evident that Cu(II) complexes posses maximum toxicity, the toxicity decreases with decrease of concentration.

Conclusion

The work concludes with the synthesis of the ligands benzofuro-2-carboxy-phenyl thiosemicarbazide and benzofuro-2-carboxy-[4'-chlorophenyl]thiosemicarbazide. Further metal complexes of Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) mono-nitrophenates. The structure of newly synthesized complexes and the ligands were established with UV-visible spectroscopy, infrared spectroscopy and magnetic studies. The magnetic moment value of Cu(II), Ni(II) and Zn(II) complexes suggested distorted octahedral and octahedral geometry. From the fungicidal activity data, it is evident that among all the metal complexes tested for their antifungal activity, Cu(II) complexes are most active fungicides. The fungicidal action of Cu(II) complexes may be explained due to inactivation of enzymes. The other metal complexes are however not much fungi toxic for the particular fungi. Generally, the fungi toxicity enhanced with increase in the dose of complex.

REFERENCES

1. G. Domagk, *Am. Rev. Tubercul. Pulmon. Dis.*, **61**, 8 (1950).
2. S. Sardari, S. Feizi, A.H. Rezayan, P. Azerang, S.M. Shahcheragh, G. Ghavami and A. Habibi, *Iran. J. Pharm. Res.*, **16**, 1128 (2017).
3. Z.A. Kaplancikli, M.D. Altintop, B. Sever, Z. Cantürk and A. Özdemir, J. Chem., **Article ID 1692540**, (2016) https://doi.org/10.1155/2016/1692540.
4. D.M. Wiles, B.A. Gingras and T. Suprunchuk, *Can. J. Chem.*, **45**, 1735 (1967); https://doi.org/10.1139/v67-282.
5. Y. Yu, D.S. Kalinowski, Z. Kovacevic, A.R. Siafakas, P.J. Jansson, C. Stefani, D.B. Lovejoy, P.C. Sharpe, P.V. Bernhardt and D.R. Richardson, *J. Med. Chem.*, **52**, 5271 (2009); https://doi.org/10.1021/jm900552r.
6. T. Khan, R. Ahmad, S. Joshi and A.R. Khan, *Der Chem. Sinica*, **6**, 1 (2015).
7. S. Padhye, Z. Afrasiabi, E. Sinn, J. Fok, K. Mehta and N. Rath, *Inorg. Chem.*, **44**, 1154 (2005); https://doi.org/10.1021/ic048214v.
8. I.H. Krakoff, E. Ercubanas, C. Tan, K. Mayer, V. Tethune and J.H. Brechenal, *Cancer Chemother. Rep.*, **58**, 207 (1974).
9. F.A. French, E.J. Blanz, S.C. Shaddix and R.W. Brockman, *Med. Chem. (N.Y.)*, **17**, 172 (1974); https://doi.org/10.1021/jm00248a006.
10. K.C. Agrawal, A.J. Lin, B.A. Booth, J.R. Wheaton and A.C. Sartorelli, *J. Med. Chem.*, **17**, 631 (1974); https://doi.org/10.1021/jm00252a012.
11. D.J. Bauer, L.S. Vincent, C.H. Kempe and A.W. Downie, *Lancet*, **20**, 494 (1964).
12. J.A. Crim and H.G. Petering, *Cancer Res.*, **27**, 1278 (1967).
13. J. Li, B.S.P. Li-mou Zheng, I. King, T. Doyle and S.-H. Chen, *Curr. Med. Chem.*, **8**, 121 (2001); https://doi.org/10.2174/0929867013373741.
14. R. Rosell, M. Tarón and A. O'Brate, *Curr. Opin. Oncol.*, **13**, 101 (2001); https://doi.org/10.1097/00001622-200103000-00004.
15. G. Pelosi, *The Open Crystallogr. J.*, **3**, 16 (2010); https://doi.org/10.2174/1874846501003010016.
16. D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar and R.G. Yerande, *Coord. Chem. Rev.*, **123**, 49 (1993); https://doi.org/10.1016/0010-8545(93)85052-6.
17. L.N. Suvarapu, A.R. Somala, J.R. Koduru, S.O. Baek and V.R. Ammireddy, *Asian J. Chem.*, **24**, 1889 (2012).
18. S.L. Mostafa, A.A. El-Asmy and M.S. El-Shahawi, *Transition Met. Chem.*, **25**, 470 (2000); https://doi.org/10.1023/A:1007074415445.
19. K.M. Ibrahim, *Synth. React. Inorg. Met.-Org. Chem.*, **23**, 1351 (1993); https://doi.org/10.1080/15533179308016691.
20. S.L. Mostafa and M.M. Bekheit, *Chem. Pharm. Bull. Japan*, **48**, 266 (2000); https://doi.org/10.1248/cpb.48.266.
21. K.M. Ibrahim, S.I. Mostafa, N. Nawar and Z.A. Younis, *Indian J. Chem.*, **43A**, 2294 (2004).
22. K.H. Reddy, *Resonance*, **4**, 67 (1999); https://doi.org/10.1007/BF02834637.
23. S.S. David and E. Meggers, *Curr. Opin. Chem. Biol.*, 12, 194 (2008; https://doi.org/10.1016/j.cbpa.2008.03.008.
24. H. Martin, R.L. Wain and E.H. Wilkinson, *Appl. Biol.*, **29**, 412 (1942); https://doi.org/10.1111/j.1744-7348.1942.tb06146.x.
25. G.A. Carter and R.L. Wain, *Ann. Appl. Biol.*, **53**, 291 (1964); https://doi.org/10.1111/j.1744-7348.1964.tb03804.x.
26. K. Kuraoka, Y. Chujo and T. Yazawa, *Chem. Commun.*, 2477 (2000); https://doi.org/10.1039/B007925L.
27. X.-Y. Wei, J.-Z. Li, Z.-H. Mao, B. Zhou and S.-Y. Qin, *Chin. J. Chem.*, **22**, 558 (2004); https://doi.org/10.1002/cjoc.20040220613.
28. U. Ndagi, N. Mhlongo and M.E. Soliman, *Drug Design, Develop. Ther.*, 11, 599 (2017); https://doi.org/10.2147/DDDT.S119488.
29. K.L. Haas and K.J. Franz, *Chem. Rev.*, **109**, 4921 (2009); https://doi.org/10.1021/cr900134a.
30. B.J. Pages, D.L. Ang, E.P. Wright and J.R. Aldrich-Wright, *Dalton Trans.*, **44**, 3505 (2015); https://doi.org/10.1039/C4DT02700K.
31. B. Singh, R.N. Singh and R.C. Aggarwal, *Polyhedron*, **4**, 401 (1985); https://doi.org/10.1016/S0277-5387(00)86999-5.
32. K.M. Ibrahim, S.I. Mostafa, N.Y. Nawar and A. Zeinab, *Indian J. Chem.*, **43A**, 2294 (2004).
33. R. Garg, M.K. Saini N. Fahmi and R.V. Singh, *Indian J. Chem.*, **44A**, 2433 (2005).
34. M.B. Halli and Z.S. Qureshi, *Indian J. Chem.*, **43A**, 2347 (2004).
35. A.A. El-Asmy and M.M. Mostafa, *Polyhedron*, **2**, 591 (1983); https://doi.org/10.1016/S0277-5387(00)81516-8.
36. D. Khanna, V. Banerjee, B.V. Agarwal and A.K. Dey, *Indian J. Chem.*, **21A**, 621 (1982).
37. M.M. Mostafa, A.A. El-Asmy and G.M. Ibrahim, *Transition Met. Chem.*, **8**, 54 (1983); https://doi.org/10.1007/BF00618800.
38. S. Rao and K.H. Reddy, *Indian J. Chem.*, **35A**, 681 (1996).
39. N.K. Dutt and N.C. Chakder, *J. Inorg. Nucl. Chem.*, **33**, 393 (1971); https://doi.org/10.1016/0022-1902(71)80381-0.
40. C.N.R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962); https://doi.org/10.1016/S0371-1951(62)80164-7.
41. B.N. Figgis and J. Lewis, Techniques of Inorganic Chemistry, Wiley Interscience, New York, Wiley, p. 66 Chap. 3 (1965).