

Synthesis, Characterization of Some Metal Complexes of 4-Acetylsemicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one

J.D. PATEL* and P.J. SHAH†

Department of Chemistry, M.B. Patel Science College, Anand-388 001, India

E-mail: purvesh23184@gmail.com

4-Acetylsemicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one (AMP-SC) was prepared and its metal chelates of Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , UO_2^{2+} and VO^{2+} were synthesized. The ligands and its metal chelates were characterized by elemental analysis, metal:ligand (M:L) stoichiometry, IR-electronic spectral studies and magnetic properties. The compounds also screened for their antimicrobial activity.

Key Words: 4-Acetylsemicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one, Spectral studies, Magnetic moment, Metal complexes, Anti-fungal activity.

INTRODUCTION

Number of 1-phenyl-2-pyrazolin-5-one derivatives has been studied for their metal complexation study¹⁻⁴. Recently the thiosemicarbazone derivatives of 4-acetyl-1-phenyl-3-methyl-2-pyrazolin-5-one have been prepared from our laboratory⁵ and studied their metal complexation properties. As the semicarbazones derivatives of 4-acetyl-1-phenyl-3-methyl-2-pyrazolin-5-one (AMP-SC)⁶⁻⁸ have not been reported so far for their complexing behaviour. Hence, the present communications comprised the work in connection with the metal complexation study (AMP-SC) shown in **Scheme-I**.

EXPERIMENTAL

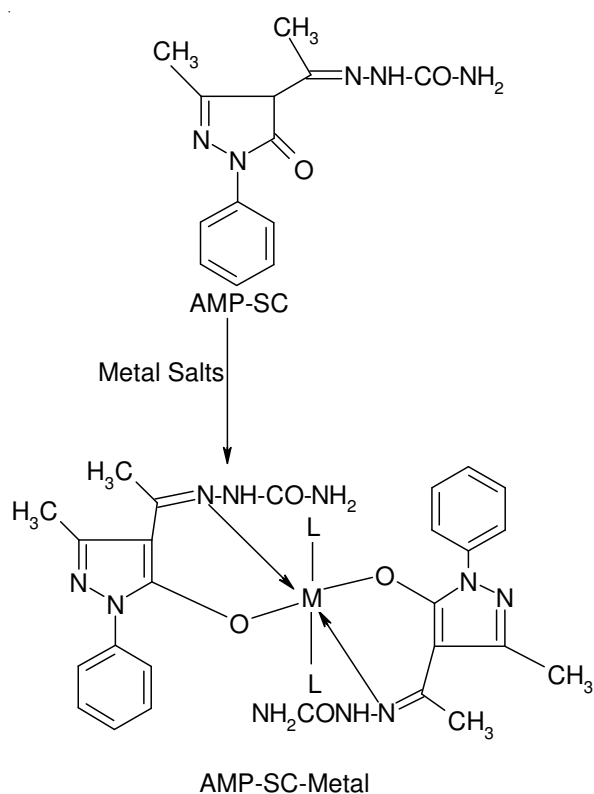
All the chemicals used in the present work were of Analytical grade. For the preparation of the metal chelates of the Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Fe^{3+} , Cr^{3+} , UO_2^{2+} and VO^{2+} metal nitrates were used. The $\text{FeSO}_4(\text{NH}_4)\text{SO}_4 \cdot \text{H}_2\text{O}$ was used in the preparation of the Fe^{2+} chelates, respectively.

Synthesis of 4-acetylsemicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one (AMP-SC): The ligand AMP-SC was prepared in two steps described below:

Preparation of 4-acetyl-2-pyrazolin-5-one: The 1-phenyl-3-methyl-2-pyrazolin-5-one (0.1 mol, 17.4 g) was placed in a flask equipped with a stirrer, separating funnel and reflux condenser. It was then dissolved in dioxane (85 mL) by heat. To the reaction mixture, calcium hydroxide (0.2 mol, 14.81 g) was added, followed by the dropwise addition of the acetyl chloride (0.1 mol) at this stage, the mixture

†Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, India

become a thick paste and its temperature also increased. The reaction mixture was then refluxed for 0.5 h. The resulting calcium complex was then decomposed by pouring it into the dilute hydrochloric acid (200 mL, 2 M). The resultant colored crystals were then collected on a Buchner-funnel and recrystallized from an acidified methanol-water mixture 20:40 (v/v)^{2,3}.



where M = Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Cr³⁺, UO₂²⁺ and VO²⁺

Scheme-I

Preparation of 4-acetylsemicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one (AMP-SC): The semicarbazone was prepared by refluxing 1:1 mol of 4-acetyl-2-pyrazolin-5-one and semicarbazide hydrochloride in methanol for 1 h. The semicarbazone of AMP, thus obtained was filtered, recrystallized from methanol and designated as AMP-SC. Yield was 72 %. It m.p. was 230 °C (uncorrected).

Elemental analysis: m.f. C₁₃H₁₅N₅O₂, m.w. (273.30); calcd. (found.) %: C 57.12 (57.0), H 5.53 (5.3), N 25.63 (24.4), IR (KBr, ν_{\max} , cm⁻¹): 3380 N-H (m, br), 3300 NH (m, s), 3052 C-H (m, br), 2957 C-H (2, sh), 1640 C=N (w, br), 1630 C=N (m, br), 1700 C=O (s, sh), 965 N-N (m, sh), 1219 O-H (m, sh), NMR (DMSO): 7.2-7.6 ppm multiplet aromatic H, 2.1-2.4 ppm (1H) singlet CH, 1.8-2.0 ppm (3H) singlet CH₃.

Synthesis of metal chelates of AMP-SC: All the metal chelates of AMP-SC were prepared in the similar manner. The general procedure is as follows: The corresponding metal nitrate (0.01 mol) was dissolved in a minimum amount of hot water (30 mL). The hot ligand (0.021 mol) solution in DMF (30 mL) (The ligand solution for Cr^{3+} and Fe^{3+} was 0.031 mol) was added dropwise with constant stirring. To the resulting mixture 2 g of sodium acetate was added and then the mixture was refluxed for 1 h. The resulting mixture thus obtained was then concentrated to half of its original volume. The product was filtered and washed several times with hot water. The product was air-dried and then kept in desiccator. The yield of all chelates were almost quantitative.

The elemental analysis for C, H and N were carried out on elemental analyzer. IR spectra of AMP-SC and its metal complexes were scanned on a Perkin-Emer 983 (USA) spectrophotometer KBr. Estimation of metal in each compound was carried out by gravimetric oxide method and EDTA titration as described by Flaschka¹. The vibrating sample magnetometer (VSM), model 7304 (4 inch electro-magnet VSM system), lakeshore crytronics, Inc., USA, was used to characterize magnetic properties of metal chelates. The diffused reflectance spectra of solid metal complexes were recorded on a Beckman-DK-2A spectrophotometer with a solid reflectance compound. The thermograms of the chelates were recorded on SDT-2960 simultaneous DSC-TGA. The electrical conductivity of all the complexes were measure in DMF using "conductivity Bridge 305" (systronics).

Antifungal activity: The fungicidal activity of all the compounds was studied at 1000 ppm concentration *in vitro* plant pathogenic organisms listed in Table-1. The antifungal activities of all the samples were measured by cup plate method. Each of the plant pathogenic strains on potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200 g, dextrose 20 g, agar 20 g and water 1 L. 5 days old cultures were employed. The compounds to be tested were suspended (1000 ppm) in a PDA medium and autoclaved at 120 °C for 15 min at 15 atm pressure. These medium were poured into sterile petri plate and the organisms were inoculated

TABLE-1
ANTIFUNGAL ACTIVITY OF AMP-SC LIGAND AND ITS METAL CHELATES

Sample	Zone of inhibition of fungus at 1000 ppm (%)						
	BT	N	RN	AN	AF	AA	AK
AMP-SC	55	54	53	63	63	67	70
AMP-SC-Cu	83	78	77	83	81	81	85
AMP-SC-Ni	80	77	75	75	73	81	80
AMP-SC-Co	65	75	75	73	78	79	85
AMP-SC-Mn	79	74	73	75	80	77	83
AMP-SC-Fe	75	64	63	77	83	83	84
AMP-SC-Fe	80	85	89	80	85	75	85

BT = *Botrydeplaia thiobromine*, N= *Nigrospora Sp.*, RN = *Rhisopus Nigricans*, AN = *Aspergillus niger*, AF = *Aeprgines funigalus*, AA = *Anida Albicans*, AK = *Andida krusegios candida grabrata* HO5.

after cooling the petri plate. The percentage inhabitation for fungi was calculated after 5 days using the formula given below.

$$\text{Percentage of inhibition} = \frac{100(X - Y)}{X}$$

where, X: Area of colony in control plate, Y: Area of colony in test plate.

RESULTS AND DISCUSSION

The parent ligand AMP-SC was amorphous powdered, soluble in various solvents like dioxane, DMSO and DMF. The results of elemental analysis of the ligand are reported in a Table-2. They are consistent with the predicted structure as **Scheme-I**. Examination of IR spectrum of AMP-SC reveals that a broad band of N-H is observed at 3380 cm^{-1} as well as 1640 cm^{-1} C=N (azomethine), 1700 cm^{-1} (C=O). The NMR data also confirm the structure of AMP-SC. The metal complexes of AMP-SC with the metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} and Cr^{3+} vary in colours. On the basis of the proposed structure as shown in **Scheme-I**, the molecular formula of the AMP-SC ligand is $\text{C}_{13}\text{H}_{15}\text{N}_5\text{O}_2$ (273.30) which upon complex ion coordinates with one central metal atom at four coordinates sites and with one water molecules. Therefore the general molecular formula of the resulting metal complex is $[\text{C}_{13}\text{H}_{15}\text{N}_5\text{O}_2]_2 \cdot \text{M} \cdot \text{H}_2\text{O}$ for divalents metal ions. This has been confirmed by results of elemental analysis of all the metal chelates and their parent ligand. The data of elemental analysis reported in Table-2 are in arrangement with the calculated values of C, H and N based on the above mentioned molecular formula of parent ligand as well as metal complex. The electrical conductivity of these complexes in acetonitrile indicates that the complexes are essentially non-electrolytes.

TABLE-2
ELEMENTAL ANALYSIS OF AMP-SC LIGAND AND ITS METAL CHELATES

Empirical formula	m.w.	Yield (%)	Elemental analysis (%)							
			C		H		N		M	
			Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
$\text{C}_{13}\text{H}_{15}\text{N}_5\text{O}_2$	273.00	72	57.12	57.34	5.53	5.23	25.63	24.98	–	–
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{Cu} \cdot 2\text{H}_2\text{O}$	644.50	70	52.69	52.61	5.77	5.92	23.63	23.52	9.91	9.89
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{Ni} \cdot 2\text{H}_2\text{O}$	639.70	65	48.69	48.84	5.34	5.08	22.84	22.26	9.16	9.52
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{Co} \cdot 2\text{H}_2\text{O}$	639.90	70	48.76	48.80	5.34	4.96	21.84	21.93	9.19	9.15
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{Mn} \cdot 2\text{H}_2\text{O}$	635.90	75	49.29	48.93	5.41	4.57	22.11	21.89	9.13	9.18
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{Fe} \cdot 2\text{H}_2\text{O}$	639.80	65	48.90	49.20	5.36	4.81	21.94	21.88	8.74	8.51
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{FeNO}_3 \cdot \text{H}_2\text{O}$	683.80	75	45.75	45.55	4.73	4.44	22.58	22.84	9.17	10.15
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{CrNO}_3 \cdot \text{H}_2\text{O}$	682.00	75	46.01	45.77	4.75	4.21	22.18	21.14	7.66	7.80
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{VO} \cdot \text{H}_2\text{O}$	629.94	75	49.44	49.39	4.79	4.15	22.18	22.00	8.07	8.05
$\text{C}_{26}\text{H}_{29}\text{N}_{10}\text{O}_4\text{UO}_2$	815.00	75	38.23	38.9	3.70	3.82	17.16	17.43	29.14	29.35

IR spectra of metal complexes reveal that all the spectra are identical in all respects. The comparison of IR spectrum of the parent ligand AMP-SC with that of its each metal complex has revealed certain characteristics differences.

One of the significant differences to be expected between the IR spectrum of the parent ligand and its metal complex is the presence of more broadened bands in the region of 3450-3100 cm^{-1} for the metal complex as the oxygen of the O-H, nitrogen of N-H of ligands forms a coordination band with the metal ions. It is noted that the ligand band at 965 cm^{-1} assigned to $\nu(\text{N-N})$, shifts to 990-1000 cm^{-1} on complexation leading further support to the involvement of nitrogen of azomethine moiety in the complex formation. The ligand band at 1700 cm^{-1} show an absorption due to O-H in the region 1250-1210 cm^{-1} . This peak is either missing or shows a significance lowering of intensity in the chelates. A strong band 960 cm^{-1} in a vanadyl complex may be assigning to $\nu(\text{V=O})$. A peak 900 cm^{-1} in the uranyl complexes may be assigned to asymmetric stretching of O=U=O moiety⁹⁻¹¹.

TABLE-3
SPECTRAL FEATURUES AND MAGNETIC MOMENT OF
AMP-SC METAL CHELATES

Metal chelates	μ_{eff} (BM)	Molar cond. $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	Electronic spectral data (cm^{-1})	Transition
AMP-SC-Cu	1.89	9.13	13175	Charge transfer
			25642	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
AMP-SC-Ni	2.92	3.74	10351	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$
			17271	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$
			30487	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$
AMP-SC-Co	4.54	3.28	10528	${}^4\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$
			19723	${}^4\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$
			23866	${}^4\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$
AMP-SC-Mn	6.04	4.45	23869	${}^6\text{A}_{1g} \rightarrow {}^6\text{A}_{2g} {}^4\text{E}_g$
			18349	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g} (4\text{G})$
			16826	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{PG})$
AMP-SC-Fe	4.92	5.85	22657	Charge transfer
			16447	${}^5\text{T}_{2g} \rightarrow {}^2\text{E}_g$
AMP-SC-Fe-NO ₃	6.81	-	25641	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$
			19157	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$
			12903	${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g} {}^4\text{E}_g$
AMP-SC-Cr-NO ₃	3.51	6.08	18587	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$
			23980	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$
			39289	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$
AMP-SC-VO	1.95	6.08	12336	$d_{xy} \rightarrow d_{xz}, d_{yz}$
			17241	$d_{xy} \rightarrow d_x^2 - y^2$
			24937	$d_{xy} \rightarrow d_z^2$
AMP-SC-UO ₂	Diamag.	3.28	-	-

Examination of data of the metal content in each compound revealed a 1:2 metal:ligand (M:L) stoichiometry in all of the complex of divalent metal ions and 1:3 for trivalent ions. Magnetic moment (μ_{eff}) of each of the metal complex is given in Table-3. Examination of these data reveals that UO_2^{2+} complex is diamagnetic, while other are paramagnetic.

The diffuse electronic spectrum of $[\text{Cu}(\text{AMP-SC})_2(\text{H}_2\text{O})_2]$ metal complex shows broad band at 15000 cm^{-1} on a strong charge transfer band at 25000 cm^{-1} . The $[\text{Ni}(\text{HL})(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]$ complex gave two absorption bands, respectively at $15601, 22996$ and $15381, 22723\text{ cm}^{-1}$ corresponding to ${}^4\text{T}_{1g} \rightarrow {}^2\text{T}_{1g}$ and ${}^4\text{T}_{1g}(\text{p})$ transitions. Thus absorption bands at the diffuse, reflectance spectra and the value of magnetic moments indicate an octahedral configuration for the $[\text{Ni}(\text{HL})(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]$ complex. The electronic spectra of Fe(III) chelates, the d-d transition appear mostly as weak bands¹³⁻¹⁶. The spectra show bands at $12000, 18000$ and 25000 cm^{-1} . These bands correspond to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G}), {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^4\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g}(\text{G})$ transition, respectively, in an octahedral stereochemistry¹⁷⁻²³.

Conductivities of all the complexes were measured in acetonitrile solvent, all the complexes were found to be non-electrolytic in nature and molar conductivity values were in the range of $3.28\text{--}22.22\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ in DMF.

The antifungal activity of all the compounds measured for various plant pathogens. Inspection of the result shown in Table-1 indicated that all compounds are good toxic for fungi. Out of all the compounds copper chelates is more toxic than other. These compounds almost inhibit the fungi about 70%. Hence, produced metal chelates can be employed as garden fungicides.

REFERENCES

1. J.P. Fackler, *J. Inorg. Chem.*, **7**, 361 (1966).
2. J.C. Bailar and D.H. Busch, *The Chemistry of Coordination Compounds*, Einhold Publishing Corporation, New York, p. 41 (1956).
3. G.H. Bamford and D.J. Lind, *Proc. Roy. Soc. Ser. A*, **302**, 169 (1969).
4. B.S. Jansen, *Acta Chem. Scand.*, **13**, 1668 (1959).
5. E. Larsen, I.H. Qureshi and J. Mollar, *Org. Mass Spectrom.*, **7**, 89 (1973).
6. D.S. Raj, J.R. Shah and P.C. Shah, *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 321 (1992).
7. S. Belaid, A. Landreau, S. Djebbar, O. Benali-Batich, M.A. Khan and G. Bouet, *Transition Met. Chem.*, **33**, 511 (2008).
8. D.S. Raj, N.J. Parmar and J.R. Shah, *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 697 (2004).
9. P.M. Parikh and J.R. Shah, *Synth. React. Met.-Org. Chem.*, **15**, 493 (1985).
10. W. Wengquing, C. Cai, C.D. Fong and W. Chinkwang, *Beijing Daxue Xuebao, Ziran Kexueben*, **1**, 47 (1982).
11. T. Qingyun and Y. Shujun, *Kuangye Geongcheng*, **7**, 53 (1987).
12. M.Y. Mirza, F.A. Nwabue and S. Ahemd, *Radiochim. Acta*, **28**, 159 (1981).
13. E. Ivanovaa, N. Iordanov, A. Terebenina, S. Mareva and G. Borisov, *Izv Khim.*, **14**, 167 (1981).
14. F.I. Labanov, A.D. Lazarev, T.D. Voronov, A.V. Stefanov, A. Ivashkin and N.V. Makarov, *Zh. Neorg. Khim.*, **27**, 2030 (1982).
15. J.P. Brunette, E.H. Rifi, M.J.F. Leroy, P. Mallo, Waton and M. Gand Prevost, *Solvent Extr. Ion Exch.*, **5**, 1017 (1987).

16. B. Wang, J. Wu, H. Zhang, P. Zhang and H. Zhang, *Fudan Xuebao Ziran Kexueban*, **28**, 24 (1989).
17. Yu. A. Zolotov and L.G. Gavrilova, *Zh. Anal. Khim.*, **25**, 813 (1970).
18. Yu. A. Zolotov, O.M. Pertrukhin and L.G. Gavrilova, *Zh. Anal. Khim.*, **32**, 1679 (1970).
19. O. Navartil and J. Smola, *Coll. Czech. Chem. Commun.*, **36**, 3549 (1971).
20. O. Navartil, *Coll. Czech. Chem. Commun.*, **36**, 2019 (1974).
21. L.-M. Li and G.-X. Xu, *Huaxuem Xuebao*, **1**, 340 (1982).
22. L.-M. Li and G.-X. Xu, *Kao Teng Hsueh Hsiao Hua Hsueh Hsueh Pao*, **2**, 12 (1981).
23. S. Umetani and M. Matsui, *Proc. Symp. Solvent Extr.*, 71 (1982)

(Received: 7 July 2009;

Accepted: 30 December 2009)

AJC-8240