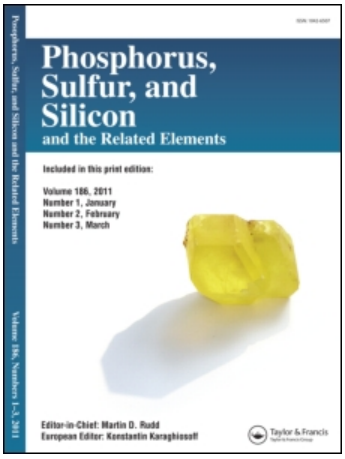

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Synthesis and Characterization of Transition Metal (Cu, Co, Fe) Complexes of 6-Methyl-5-arylhydrazono-2-thio-4-oxo-pyrimidine Ligand

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The article deals with a study to synthesize transition metal complexes of copper, cobalt, and iron with the ligand 6-methyl-5-arylhydrazono-2-thio-4-oxo-pyrimidine (MATOPyr). The synthesized ligand and all metal complexes were characterized by elemental analysis, XRD, SEM, FTIR, ^{1}HNMR, UV-VIS, magnetic spectral studies, and Mössbauer measurements. The morphology of the ligand along with the complexes of all three metals was also deduced.

Keywords Cobalt complex; copper complex; iron complex; pyrimidine

INTRODUCTION

Pyrimidine and heterocyclic annulated pyrimidine systems undoubtedly belong to the most ubiquitous heterocycles in nature.[1] They have attracted considerable attention of both synthetic and medicinal chemists by virtue of their interesting biological activities[2] and immense synthetic potential for the constructions of many pharmacologically important novel heterocycles.[3] In particular, this type of pyrimidine derivative, an important class of nitrogen-containing fused heterocycles,[4–8] has received extensive interest in the recent past owing to its wide spectrum of biological activity and clinical applications.[9] Pyrimidine derivatives constitute a very important class of compounds because they are components of nucleic acids and synthesized as a modulator of antitumor drug activity,[10] antioxidants,[11] antiplatelet,[12]

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antiviral,[13,14] antifungal,[15] and hepatoprotective[16] agents. Metal complexes of some pyrimidine derivatives have been found in some instances to have enhanced or modified their activity in comparison to the non-coordinated ligand. Some transitional metal complexes with a pyrimidine derivative have been used as antitumor agents.[17] Moreover, transition metal complexes containing a pyrimidine ligand are commonly found in biological studies and play important roles in processes such as the catalysis of drug interaction with biomolecules[18,19] and organic transformations.[20] The coordination properties of pyrimidine are important in understanding the role of metal ions in biological systems,[21] and its physicochemical importance creates a great interest in their complexation.[22] In view of the broad-spectrum importance associated with these metal complexes, it was considered worthwhile to prepare some novel and unique complexes derived from hitherto uninvestigated pyrimidines as the complexing agents. In this article, we have synthesized substituted aniline with pyrimidine derivatives and achieved their complexation with copper, cobalt, and iron metal salts. The prepared molecules possess hydrazono, carbonyl, and thionyl functional groups as potential binding sites for metal ions. This article reports the synthesis and structural elucidation of Cu (II), Co (II), and Fe (III) metal complexes with this ligand.

RESULTS AND DISCUSSION

Spectro-analytical studies viz FTIR, ^{1}H NMR, UV-VIS, magnetic susceptibility, XRD, SEM, elemental analysis, and Mössbauer measurements corroborated the structure of all the synthesized compounds. The synthetic and analytical data of resulting complexes are recorded in Table I. For metal, carbon, hydrogen, nitrogen, and sulfur, theoretical values agree with the experimental values within limit of experimental error.

X-Ray Diffraction and SEM Studies

The prepared samples were not suitable for single-crystal growth. The samples were characterized at room temperature by X-ray diffraction using Cu Kα radiation. X-ray diffraction studies of the complexes Cu (MATOPyr) Cl_2, Co (MATOPyr) Cl_2, and Fe (MATOPyr) Cl_3 are indicative of their crystalline nature. The diffraction patterns have been successfully indexed.

TABLE I Analytical Data and Physical Properties for the Ligand and Its Metal Complexes

Complex	Empirical formula	Formula Mass	Yield %	Mp °C	Elemental analysis Calculated (Found)% C	H	N	S	Metal salt Analysis
Ligand	($C_{13}H_{13}N_5O_3S$)	319.33	65	200	48.89 (48.88)	4.10 (4.09)	21.93 (21.92)	10.04 (10.03)	–
Cu complex	(Cu $C_{13}H_{13}N_5O_3SCl_2$)	453.79	60	240	40.78 (40.77)	3.42 (3.41)	18.29 (18.28)	8.37 (8.36)	16.60 (16.59)
Co complex	(Co $C_{13}H_{13}N_5O_3SCl_2$)	449.17	63	220	41.28 (41.29)	3.28 (3.45)	18.51 (18.50)	8.69 (8.68)	15.58 (15.57)
Fe Complex	(Fe $C_{13}H_{13}N_5O_3SCl_3$)	481.54	61	230	34.08 (35.0)	2.91 (2.94)	14.54 (14.53)	6.66 (6.65)	12.48 (12.52)

	a	b	c
Cu (MATOPyr)Cl_2	7.23	6.29	5.52
Co(MATOPyr)Cl_2	8.16	12.12	8.60
Fe(MATOPyr)Cl_3	10.72	8.88	7.31

These values indicate an orthorhombic crystal lattice for all complexes. The XRD pattern of sample Fe (MATOPyr) Cl_3 is shown in Figure 1. The lattice constants were also calculated. The XRD peaks of a single phase were indexed, and grain sizes were also calculated for the complexes. X-ray powdered diffraction studies of the three complexes were recorded; the prominent lines were indexed by Ito's method[23] and computed in Table II.

According to Scherrer's equation,[24] the grain size is given by $t = 0.9\ \lambda/B\ \text{Cos}\ \theta$, where t is the crystal thickness (same units as λ), B is half width (in radians) of the diffraction line, θ is the Bragg angle, and λ is the wavelength. The grain size corresponding to each diffraction maxima can be determined from the measurement of the half width of the diffraction peak. The values for Cu (MATOPyr) Cl_2, Co (MATOPyr) Cl_2, and Fe (MATOPyr) Cl_3 are 51.02, 49.76, and 33.89 nm, respectively.

The SEM pictures of the samples are shown in Figure 2. From the figure, it can be seen that the average length of crystals for the samples ranges from 1.7–14 μm as average particle size. Also, there are some void spaces. The surface morphology changes with changes in

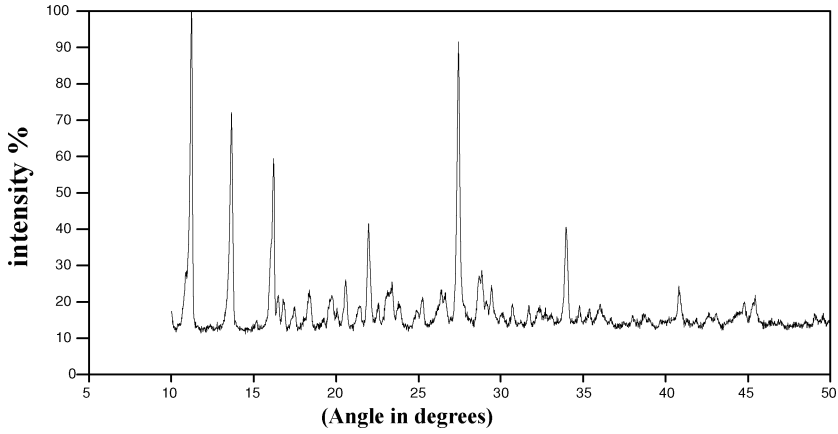
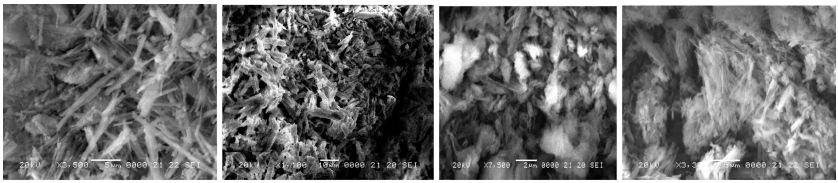


FIGURE 1 XRD pattern of Fe (MATO Pyr).

TABLE II X-Ray Powdered Diffraction Data of All Complexes

	Intensity	Angle°	d(Å)	Q_{obs}(1/d2)	Q_{calcd}	hkl
Cu (MATOPyr) Cl_2						
1	100	11.20	7.834	0.027	0.025	010
2	71.99	13.62	6.448	0.034	0.032	001
3	58.75	16.81	5.437	0.076	0.077	111
4	23.09	18.36	4.794	0.103	0.100	020
5	24.69	23.77	3.779	0.176	0.177	220
6	20.88	24.81	3.716	0.192	0.197	310
7	91.20	27.42	3.563	0.352	0.357	411
8	28.13	28.93	3.228	0.423	0.422	140
9	39.20	33.97	3.064	0.432	0.436	041
10	20.88	44.87	2.62	0.554	0.550	014
Co(MATOPyr)Cl_2						
1	36.56	12.37	7.146	0.019	0.019	011
2	36.64	14.90	5.938	0.028	0.022	101
3	37.86	22.41	3.962	0.063	0.068	010
4	66.82	24.62	3.611	0.076	0.073	201
5	36.54	31.74	2.815	0.126	0.120	212
6	47.38	32.40	2.759	0.131	0.138	121
7	53.99	33.77	2.750	0.132	0.136	103
8	99.18	37.81	2.376	0.149	0.143	310
9	46.08	39.51	2.278	0.177	0.179	320
10	39.87	54.45	1.683	0.240	0.243	400
Fe(MATOPyr)Cl_3						
1	6.20	14.95	5.918	0.035	0.039	111
2	51.10	16.4	5.398	0.041	0.041	011
3	99.13	23.76	3.740	0.056	0.053	201
4	6.30	27.93	3.190	0.067	0.069	021
5	14.70	28.74	3.102	0.081	0.074	002
6	8.77	29.5	3.024	0.095	0.096	112
7	67.73	33.64	2.660	0.114	0.114	030
8	57.34	34.59	2.590	0.123	0.122	130
9	96.35	39.44	2.281	0.172	0.177	103
10	76.10	44.21	2.046	0.187	0.188	113
11	35.27	54.38	1.685	0.231	0.230	141
12	5.96	63.32	1.467	0.313	0.312	014

the chemical environment of the samples. These images showed the large number of regular and irregular shapes of particles. The values of particle size measured from SEM pictures are 14.0, 12.5, 1.7, and 4.0 μm for ligand (MATOPyr), complex Cu (MATOPyr) Cl_2, complex Co (MATOPyr) Cl_2, and complex Fe (MATOPyr) Cl_3, respectively. It is clear from the results that the average grain size estimated by SEM is larger than the average grain size measured by XRD pattern.



(a) (b) (c) (d)

FIGURE 2 SEM pictures of the ligand (a) and copper (b), cobalt (c), and iron (d) complexes.

IR Spectra

The IR spectra of all samples were performed at field between 4000–300 cm^{-1}, along with tentative assignments. The infrared spectroscopic data of the ligand show a very strong band at 1733 cm^{-1}, which may be attributed to ν (C=O). Upon complexation, the band at 1733 cm^{-1} has shifted to a region of 1720–1701 cm^{-1}, showing that the carbonyl oxygen is involved in coordination.[25] This is clear evidence for coordination by carbonyl oxygen. The band due to ν (N-H) shifts to lower wave numbers by about 20–30 cm^{-1} in all complexes, and this band becomes weak in the complexes, suggesting the coordination of nitrogen of the ν (N-H) group.[26] In addition, ν (C=N) mode may be coupled with ν (C=S) and ν (NO_2) to give an intense band; bands were observed at 1565–1494 cm^{-1}, 1249–1128 cm^{-1}, 1534–1527 cm^{-1}, and 1335–1328 cm^{-1}.[27] The other low-intensity bands of 588–559 cm^{-1} ν (M-N), 445–430 cm^{-1} ν (M-O), and 370–300 cm^{-1} ν (M-Cl) were also reported.[28–30] Infrared spectral data of complexes are presented in Table III.

Electronic Spectra and Magnetic Studies

The effective magnetic susceptibility values of 1.8, 4.7, and 5.8 BM were observed for the copper, cobalt, and iron complexes, respectively (see

TABLE III Characteristic IR Spectral Data of the Ligand and Metal Complexes

Complex	C=O	N-H	C=N	C=S	NO_2	M-N	M-O	M-Cl
Ligand (MATOPyr)	1733	3470	1565	1222	1530,1332	–	–	–
Cu(MATOPyr)Cl_2	1711	3450	1521	1130	1528,1331	588	445	315
Co(MATOPyr)Cl_2	1720	3449	1494	1128	1534,1328	559	430	300
Fe(MATOPyr)Cl_3	1701	3465	1529	1249	1527,1335	581	441	370

TABLE IV Magnetic Susceptibility and Electronic Spectral Data

Complex	μ (BM)	λ_{max}(nm)
Ligand (MATOPyr)	–	218,242, 327
Cu (MATOPyr) Cl_2	1.8	300,410, 658
Co(MATOPyr) Cl_2	4.7	320,520, 650
Fe (MATOPyr) Cl_3	5.8	454,518

Table IV). These values lay within the range for respective high spin octahedral complexes.[31] The electronic spectrum of the ligand showed broad bands at 218, 242, and 327 nm; the first two absorption bands may be assigned to n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions[32] of >C=O and >C=N moieties, and the third absorption band may be due to $\pi \rightarrow \pi^*$ of pyrimidine ring. Upon complexation, these transitions shifted to lower and higher energy regions compared to the free ligand, confirming coordination of the ligand to metal. In the copper complex, two intense bands at 300 nm and 410 nm were observed due to intra-ligand and charge transfer transitions, and third broad band was observed at 658 nm, which may be assigned to $^2E_g \rightarrow {}^2T_{2g}$, showing the presence of octahedral geometry.[33] In the spectrum of the cobalt complex, one band was observed at 320 nm due to charge transfer transition, and two distinct absorption bands were observed at 650 nm and 520 nm, which are assignable to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, indicating an octahedral geometry.[34] The electronic spectrum of the iron complex shows two absorption bands at 588 nm and 454 nm, corresponding to $^6A_{1g}(S) \rightarrow {}^4T_{1g}$ (F) and $^6A_{1g}(S) \rightarrow {}^4T_{2g}$ (F) electronic transitions,[35] suggesting a high spin octahedral field around the Fe ion. The octahedral geometry of all metal complexes is achieved by a coordinated ligand, chloride ions, or a bidentate pyrimidine ligand. The effective magnetic susceptibility values obtained for all samples support the above electronic transitions. The absorption and strength of electronic spectral data in the spectrum of the ligand and complexes are different, indicating that the ligand coordinated to metal ions, which is in accordance with the results of IR and ^{1}H NMR spectral data.

Mössbauer Studies

The Mössbauer spectrum for Fe (MATOPyr) Cl_3 is shown in Figure 3. This spectrum is a least-squares fit with a superposition of two doublets and one singlet, all with Lorentzian line shape. The fitted parameters

TABLE V Mössbauer Spectral Data

Sample	FWHM (mm/s)	Isomer shift (mm/s)	QS (mm/s)	% Area
$Fe^{2+(a)}$	0.254 ± 0.074	1.217 ± 0.005	3.09 ± 0.050	35.6
$Fe^{2+(b)}$	0.373 ± 0.029	1.213 ± 0.006	2.89 ± 0.112	53.3
Fe^{3+}	0.588 ± 0.089	0.341 ± 0.032	–	11.1

are given in the Table V. According to the collected data presented in the table, the percentage of the Fe complex is 88.9%. The isomer shift of 1.217 ± 0.005 mm/s (35.6%), 1.213 ± 0.006 (53.3%) corresponds to the expected value for an octahedral Fe complex, as in a previously described complex,[36] which exhibits distorted octahedral symmetry with an isomer shift of 1.212 mm/s and quadrapole splitting of 3.01 mm/s. In the present case, Fe (II) exist in two chemical environments. $Fe^{2+(a)}$ with an isomer shift of 1.217 mm/s and $Fe^{2+(b)}$ with an isomer shift of 1.213 mm/s is predominant in the sample (35.526% and 53.271%, respectively). The presence of Fe (III) (11.1%) is well characterized by the isomer shift of 0.341 ± 0.032 mm/s.

^{1}H NMR Spectra

The spectrum of the ligand shows different peaks at 2.09(s), 10.38(s), and 7.20–8.40 (m) (Table VI). These peaks are attributed to –CH3, –NH, and aromatic protons, respectively. The signals due to the –NH proton

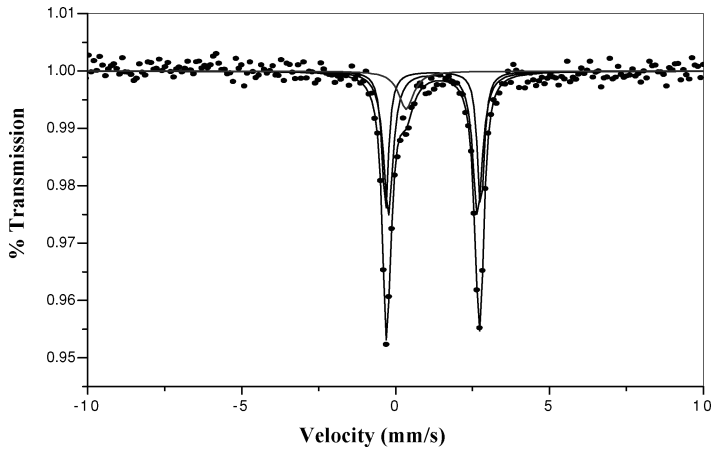


FIGURE 3 Mössbauer spectrum for Fe (MATOPyr) Cl_3.

TABLE VI The ^{1}HNMR Spectra of the Ligand and Complexes

Complex	δ (ppm) ($CDCl_3$)	Assignments
Ligand (MATOPyr)	2.09(*s*, 3*H*)	$-CH_3$
	10.38(*s*, 1*H*)	–NH
	7.20–8.40(*m*, 2*H*)	Aromatic Protons (H)
Cu (MATOPyr) Cl_2	2.09(*s*, 3*H*)	$-CH_3$
	10.21(*s*, 1*H*)	–NH
	7.20–8.33(*m*, 2*H*)	Aromatic Protons (H)
Co(MATOPyr) Cl_2	2.55(*s*, 3*H*)	$-CH_3$
	10.29(*s*, 1*H*)	–NH
	7.60–8.31(*m*, 2*H*)	Aromatic Protons (H)
Fe (MATOPyr) Cl_3	2.69(*s*, 3*H*)	$-CH_3$
	10.20(*s*, 1*H*)	–NH
	7.11–8.24(*m*, 2*H*)	Aromatic Protons (H)

S–singlet, m–multiplet.

are shifted downfield in the spectra of the Cu complex, Co complex, and Fe complex, indicating the coordination of the ligand through the nitrogen of –NH groups to the metal ions.

Suggested Structure of the Complexes

On the basis of the above studies and discussion, Figure 4 shows the suggested structure for the metal complexes. Based on formula mass determination, effective magnetic susceptibilities, and electronic and IR spectra, a general structure (Figure 4) is assigned for all the complexes.

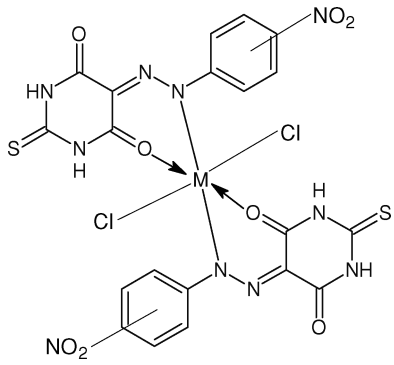


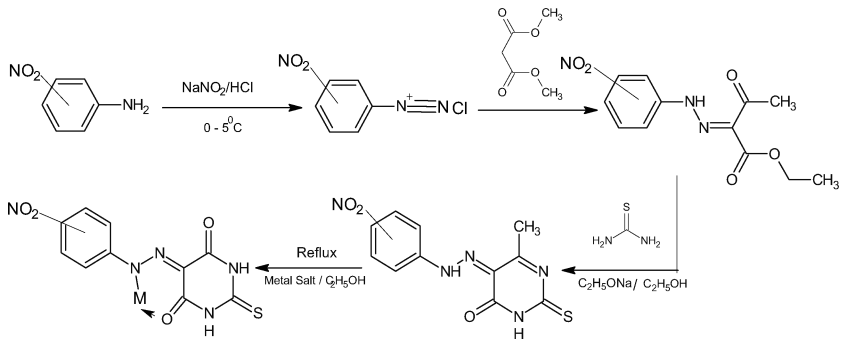
FIGURE 4 Structure of the complex (M=Cu, Co, and Fe).

EXPERIMENTAL

All the reagents used in the preparations of the ligand and the metal complexes were of pure grade (Merck). The solvent used for the synthesis of ligands and metal complexes were distilled before use. The elemental analysis (C, H, N, and S) of the samples was performed using a Carlo Erba elemental analyzer. Melting points were determined in open capillary tubes using an electric melting point apparatus and are uncorrected (see Table I). The X-ray diffraction (XRD) pattern was obtained using a Philips PW 3040/60 X-ray powder diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.54A^{\circ}$) having an operating voltage of 40 kV and current of 100 mA. The surface morphology of the sample was examined using scanning electron microscopy (SEM) on a JEOL JSM 5600 SEM instrument. The infrared absorption spectra of the ligand and complexes were measured at room temperature, in the wave number range 4000 to 300 cm^{-1} on a Jasco FTIR-300 spectrometer using the KBr pellet technique. The samples were investigated as fine particles, which were mixed with KBr in the ratio (2:200 mg powder:KBr respectively); the weighed mixture was then subjected to a pressure of 5 t/cm^2 to produce clear homogeneous discs. Electronic spectra were recorded in methanol on a UV-1700 SHIMADZU spectrometer. The magnetic susceptibility of the complexes was measured on Gouy balance using Hg $[Co(NCS)_4]$ as a calibrant at room temperature. ^1H NMR spectra (δ, ppm) were recorded on a 300 MHz Bruker spectrometer with $CDCl_3$ as a solvent. The Mössbauer measurements were carried out using a standard PC-based spectrometer equipped with a Weissel velocity drive operating in the constant acceleration mode. The data was fitted with the NORMOS-SITE program, and the obtained parameters are with respect to natural iron.

Synthesis of the Ligand (6-Methyl-5-arylhydrazono-2-thio-4 -oxo-pyrimidine)

In a 250 mL beaker, the pertinent aniline (0.01 mol) was dissolved in a mixture of concentrated hydrochloric acid (3 mL) and water (4 mL) and cooled to 0–5°C in an ice bath. To this, a cold aqueous solution of sodium nitrite (0.01 mol) was then added dropwise. The diazonium salt obtained was filtered into a cold mixture of sodium acetate (7.0 g) and ethyl acetoacetate (0.01 mol) in ethanol (25 mL). The resulting solid obtained was filtered, washed with water, and dried to obtain pure crystals of 1-ethoxy-2-arylhydrazono-butane-1,3-dione. Then equimolar quantities of a 1-ethoxy-2-arylhydrazono-butane-1,3-dione (0.01 mol) and thiourea (0.01 mol) were dissolved in freshly prepared



SCHEME 1 Schematic overview of synthetic strategy for ligand and metal complexes, i.e., M=Cu, Co, and Fe.

sodium ethoxide (10.0 mL) in a 250 mL round bottomed flask fitted with a reflux condenser. All the contents were refluxed for 30 min. The mixture containing the precipitate was cooled in ice, filtered, and dried in vacuo.

Synthesis of the Metal Complexes

In a 250 mL beaker, 6-methyl-5-arylhydrazono-2-thio-4-oxo-pyrimidine (1.24 mol) was dissolved in pure ethyl alcohol (10 mL). Then at a room temperature, the solution of copper, cobalt, and iron metal chloride (1.24 mol) was added dropwise with constant stirring into the ligand solution. A green precipitate of copper complex, pink precipitate of cobalt complex, and yellow precipitate of iron metal complexes were obtained. The precipitates were collected by filtration, washed with alcohol, and dried under vacuum overnight. The copper, cobalt, and iron complexes were formed in more than 60% yield. The purification of the products was done under reduced pressure, and the residue was recrystallized from ethanol, resulting in crystals of the pure compounds (Scheme 1). In all complexes, the presence of copper, cobalt, and iron is confirmed by X-ray fluorescence (XRF) and X-ray diffraction (XRD).

REFERENCES

[1] P. Sharma, N. Rane, and P. Pandey, *Arch. Pharm.*, **339,** 572 (2006).
[2] E. Lunt, In *Comprehensive Organic Chemistry*, D. Barton and W. D. Ollis, Eds. (Pergamon, Oxford, UK, 1979), Vol. 4, p. 493.
[3] J. D. Brown, In *Comprehensive Heterocyclic Chemistry*, A. R. Katrizky and C. W. Rees, Eds., (Pergamon, Oxford, UK, 1984), Vol. 3, p. 57.
[4] D. J. Brown, R. F. Evans,W. D. Cowden, M. D. Fenn, Eds., *The Pyrimidines* (Wiley, New York, 1994).

[5] D. K. Hurst, Ed., *An Introduction to the Chemistry and Biochemistry of Pyrimidines, Purines andPteridines* (John Wiley & Sons, London, 1980).
[6] J. T. Sharp, *Comprehensive Heterocyclic Chemistry*, (Pergamon, Oxford, UK, 1984).
[7] J. W. H. Wattheyand J. L. Stanton, Eds., *The Chemistry of Heterocyclic Compounds*, (John Wiley and Sons, New York, 1984).
[8] S. B. Larson, Y. S. Sanghvi, G. R. Revankar, and R. K. Robins, *Acta Cryst*., **C45,** 1194 (1989).
[9] F. F. Solca, A. Baum, E. Langkopf, G. Dahmann, K. H. Heider, F. Himmelsbach, J. C. A. Van Meel, *J. Pharmacol. Exp. Ther.*, **311,** 502 (2004).
[10] N. J. Curtin, H. C. Barlow, K. J. Bowman, A. H. Calvert, R. Davision, B. T. Golding, B. Huang, P. J. Loughlin, D. R. Nawell, P. G. Smith, and R. J. Griffin, *J. Med. Chem.*, **47,** 4905 (2004).
[11] J. P. De la Cruz, C. Olveira, J. A. Gonzalez-Correa, A. Benitez, and F. Sanchez de la Cuesta, *Gen. Pharmacol.*, **27,** 855 (1996).
[12] G. Born and C. Patrono, *Br. J. Pharmacol.*, **147,** 241 (2006).
[13] Y. S. Sanghvi, S. B. Larson, S. S. Matsumoto, L. D. Nord, F. D. Smee, R. C. Willis, T. H. Avery, R. K. Robins, and G. R. Revankar, *J. Med. Chem.*, **32,** 629 (1989).
[14] R. B. Tenser, A. Gaydos, K. A. Hay, *Antimicrob. Agents Chemother.*, **45,** 3657 (2001).
[15] J. Cieplik, J. Pluta, and O. Gubrynowicz, *Acta. Pol. Pharm.*, **60,** 487 (2003).
[16] V. J. Ram, A. Goel, S. Sarkhel, and P. R. Maulik, *Bioorg. Med. Chem.*, **10,** 1257 (2002).
[17] R. Kivekas, E. Colacio, J. Ruiz, J. D. Lopez, and P. Leon, *Inorg. Chim. Acta*, **159,** 103 (1989).
[18] A. K. Rao, P. Venkataiah, H. B. Bathina, and M. S. Mohan, *J. Coord. Chem.*, **20,** 69 (1989).
[19] H. Sigel and A. E. Matin, *Chem. Rev.*, **82,** 385 (1982).
[20] R. A. Krause and K. Krause, *Inorg. Chem.*, **23,** 2195 (1984).
[21] S. I. M. A. Kabil, E. M. Saad, and A. A.El-Asmy, *J. Coord. Chem.*, **59,** 279 (2006).
[22] P. O. Lumme and H. Knuuttila, *Polyhedron*, **14,** 1553 (1995).
[23] L. V. Azaroff and M. J. Buerger, *The Powder Methods in X-Ray Crystallography*, vol. 119, (McGraw Hill, New York, 1958).
[24] B. D. Cullity, *Element of X-Ray Diffraction*, 2nd ed. (Addison-Wesley Publishing Company, Philippines, 1978).
[25] S. Chandra and S. D. Sharma, *Transition Met. Chem.*, **27,** 732 (2002).
[26] M. B. Halli and Z. S. Qureshi, *Indian J. Chem.*, **43A,** 2347 (2004).
[27] C. Lodeiro, R. Basitida, E. Bertolo, A. Macias, and R. Rodriguez, *Transition Met. Chem.*, **28,** 388 (2003).
[28] M. T. H. Tarafder, T.-J. Khoo, K. A. Crouse, A. M. Ali, B. M. Yamin, and H.-K. Fun, *Polyhedron*, **21,** 2691 (2002).
[29] I. Demir and A. I.Pekacar, *Synt. React. Inorg. Met. Org. Nano-Met. Chem.*, **35,** 825 (2005).
[30] M. Satish, M. P Annigeri, M. P. Sathisha, and V. K. Revankar, *Transition Met. Chem.*, **31,** 81 (2007).
[31] N. Raman, S. Ravichandra, and C. Thangaaraja, *J. Chem. Sci.*, **116,** 215 (2004).
[32] J. Losada, I.delPeso, and L. Beyer, *Transition Met. Chem.*, **25,** 112 (2000).
[33] O. Z.Yesilel and H. Olmez, *Transition Met. Chem.*, **30,** 992 (2005).
[34] K. M. Ibrahim, S. I. Mostafa, N. Nawar, and Z. A. Younis, *Indian J. Chem.*, **43A,** 2294 (2004).
[35] B. N. Figgis, *Introduction to Ligand Fields* (John Wiley and Sons, New York, 1996).
[36] A. C. Massabni, P. P. Corbi, P. Melnikov, M. A. Zacharias, and H. R. Rechenberg, *J. Coord. Chem.*, **57,** 1225 (2004).