Asian Journal of Chemistry Vol. 11, No. 3 (1999), 694–698

Metal Complexes with Substituted Biphenyls

RAJ RANJAN JHA* D.K. JHA† and J.P. MISHRA
Department of Chemsistry
Ranchi University, Ranchi-843 008, India

Metal complexes of the type [MLX_2] where M = Co(II) Ni(II) and Cu(II), L = 3,3′-dimethyl-4,4′-bis(benzoylthiourea) biphenyl or 3,3′-dimethyl-4,4′-bis-(thiocarbamoyl) biphenyl and X = Cl^-, Br^-, NO_3^- and ClO_4^- have been isolated from the neutral medium. octahedral geometry for the complexes has been proposed on the basis of elemental analysis, magnetic moment and spectral studies. The coordination of the metal ions to the ligand through sulphur and carbamoyl oxygen atom in the case of formal ligand whereas through sulphur and carbamoyl nitrogen atom to the later ligand has been proposed basing on IR spectra. Fungicidal screening of the complexes shows them to be active against *Aspergillus niger, Fusarium oxysporium* and *Helminthosporium oryzae.*

INTRODUCTION

Metal complexes with ligands containing sulphur as a donor atom have been found useful as potential drugs[1–4]. We report here such sulphur complexes of Co(II), Ni(II) and Cu(II) with 3,3′-dimethyl 4,4′-bis(benzoylthiourea) biphenyl and 3,3′-dimethyl-4,4′ bis (thiocarbamoyl) biphenyl along with their fungicidal screening.

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade.

The ligands 3,3′-dimethyl 4,4′-bis (benzoylthiourea) biphenyl (DMBBTuBp) and 3,3′-dimethyl 4,4′-bis(thiocarbamoyl) biphenyl (DMBTcBp) were prepared by adopting the literature method[5]. The ligands were recrystallised from ethanol-DMF mixture.

Preparation of the Complexes

Ethanolic solution of the appropriate metal(II) salts were added to the DMF solution of the ligand in 1:1 molar ratio. The resulting mixture was refluxed in the water bath for 3 h and cooled overnight. Solids obtained were filtered, washed with ethanol and dried *in vacuo* for 24 h.

The metal and sulphur contents of the complexes were analysed according to the standard method[6]. Nitrogen was determined by semimicro combustion process. The analytical data are recorded in Table-1.

---

†Department of Chemistry, Lunglei Government College, Lunglei, Mizoram, India.

Magnetic susceptibility measurements were carried out on solid samples by Gouy method using $Hg[Co(CNS)_4]$ as a calibrant at room temperature. IR spectra were recorded on a Perkin-Elmer-398 spectrophotometer in KBr pellets. Electronic spectra were recorded in DMF on a Beckmann-35 double beam spectrophotometer.

TABLE-1
ANALYTICAL DATA OF METAL COMPLEXES

Compound/Colour	μ_{eff} B.M.	Found (Calcd.) %		
		M	S	N
[$C_{30}H_{26}N_4S_2O_2$(BMMBTuBp)]	—	—	11.98	10.28
Yellow			(11.90)	(10.40)
[Cu(DMBBTuBp)Cl_2]	1.72	9.27	9.75	8.24
Silver grey		(9.38)	(9.52)	(8.33)
[Cu(DMBBTuBp)Br_2]	1.72	8.02	8.25	7.32
Dark grey		(8.27)	(8.41)	(7..36)
[Cu(DMBBTuBp)$(NO_3)_2$]	1.73	8.42	8.72	10.45
Grey		(8.69)	(8.83)	(11.58)
[Cu(DMBBTuBp)$(ClO_4)_2$]	1.72	7.76	8.02	6.98
Palmolive green		(7.86)	(7.99)	(6.99)
[Ni(DMBBTuBp)Cl_2]	2.65	8.68	9.46	8.22
Green		(8.83)	(9.58)	(8.38)
[Ni(DMBBTuBp)Br_2]	2.68	7.52	8.36	7.10
Pale Green		(7.78)	(8.44)	(7.38)
[Ni(DMBBTuBp)$(NO_3)_2$]	2.58	8.13	8.59	11.32
Deep Green		(8.18)	(8.88)	(11.65)
[Ni(DMBBTuBp)$(ClO_4)_2$]	2.66	7.31	7.92	6.87
Mushroom		(7.40)	(8.03)	(7.02)
[Co(DMBBTuBp)Cl_2]	4.35	8.59	9.42	8.02
Grey		(8.83)	(9.58)	(8.38)
[Co(DMBBTuBp)Br_2]	4.50	7.65	8.32	7.23
Light Grey		(7.78)	(8.44)	(7.38)
[Co(DMBBTuBp)$(NO_3)_2$]	4.45	8.12	8.72	11.12
Silver Grey		(818)	(8.88)	(11.65)
[Co(DMBBTuBp)$(ClO_4)_2$]	4.42	7.32	8.09	6.77
Dull pink		(7.40)	(8.03)	(7.02)
$C_{16}H_{18}N_4S_2$(DMBTcBp)	—	—	19.31	16.85
White			(19.39)	(16.96)
[Cu(DMBTcBp)Cl_2]	1.73	13.52	13.63	11.78
Dirty green		(13.58)	(13.79)	(12.06)
[Cu(DMBTcBp)Br_2]	1.75	11.27	11.48	10.13
Chocolate		(11.39)	(11.57)	(10.43)
[Cu(DMBTcBp)$(NO_3)_2$]	1.74	12.14	12.12	16.04
Green		(12.19)	(12.38)	(16.24)

Compound/Colour	μ_{eff} B.M.	Found (Calcd.) %		
$[Cu(DMBTcBp)(ClO_4)_2]$ Grey	1.79	10.56 (10.62)	10.61 (10.79)	9.12 (9.24)
$[Ni(DMBTcBp)Cl_2]$ Dirty green	3.21	12.65 (12.82)	13.87 (13.91)	12.08 (12.17)
$[Ni(DMBTcBp)Br_2]$ Green	3.23	10.65 (10.74)	11.55 (11.65)	10.06 (10.20)
$[Ni(DMBTcBp)(NO_3)_2]$ Dirty green	3.25	11.37 (11.50)	12.36 (12.47)	16.25 (16.37)
$Ni(DMBTcBp)(ClO_4)_2]$ Greenish yellow	3.20	9.98 (10.01)	10.77 (10.86)	9.37 (9.50)
$[Co(DMBTcBp)Cl_2]$ Bluish green	3.88	12.66 (12.82)	13.65 (13.91)	12.09 (12.17)
$[Co(DMBTcBp)Br_2]$ Blue	3.85	10.52 (10.74)	11.51 (11.65)	10.01 (10.20)
$[Co(DMBTcBp)(NO_3)_2]$ Brown	3.86	11.41 (11.50)	12.41 (12.47)	15.98 (16.37)
$[Co(DMBTcBp)(ClO_4)_2]$ Grey	3.82	9.89 (10.01)	10.59 (10.86)	9.35 (9.50)

RESULTS AND DISCUSSION

All the complexes are amorphous, high melting and insoluble in water and common organic solvents. Freshly prepared samples are feebly soluble in DMF and DMSO. Low conductance values observed for all the complexes indicate that they are non-electrolytes.

The infrared spectrum of the former ligand shows a broad band in the region 3300–3000 cm^{-1} which arises due to overlap of ν(NH) vibrations with the ν(CH) vibrations of the benzidine ring[7, 8]. This band does not undergo any shift in the metal complexes suggesting that the NH group does not participate in coordination. However, in the IR spectra of the latter ligand in the higher frequency region, there are three vibrational bands at 3340, 3240 and 3120 cm^{-1}. The former two bands can be attributed to ν(NH) and ν(NH_2) vibrations respectively. These bands disappear in the metal complexes and a broad band appears in the region 3400–3200 cm^{-1} suggesting the coordination of ν(NH) group to the metal ion. The latter band which almost remains unaffected in the metal complexes may be due to ν(CH) vibration of the biphenyl groups.

A strong and sharp band appears in the former ligand spectrum at 1680 cm^{-1} which may be assigned to ν(C=O)[9]. In the meta complexes, the band shifts and appears at *ca.* 1630 cm^{-1}. The lowering of this band in the metal complexes suggests the coordination of C=O group[10]. In the latter ligand spectra in the region 2600–2500 cm^{-1} the band for ν(S—H) is absent, but a strong band is observed 1385 cm^{-1} which can be assigned to ν(C=S) of thiocarbamide group. Further the band appearing at *ca.* 720 cm^{-1} in both the ligand spectra which has got the major contribution from ν(C=S) mode, shifts to 700 cm^{-1} in the metal complexes. This marked shift suggests the coordination of sulphur atoms to the metal ion[11].

In the former ligand a strong band of moderate width appears at 1170 cm^{-1} which may be assigned to ν(C—N) mode. At the same time the ν(C—N) band shifts to higher frequency region in the metal complexes and appears at 1180 cm^{-1}. In the latter ligand another band of strong and sharp intensity is noticed at *ca.* 1600 cm^{-1}. This band can be attributed to the coupled vibrations of ν(C—N) and ν(NH) deformation. Coordination of metal through nitrogen will result in the increase in ν(C—N) stretching frequency[9]. In all the metal complexes the C—N is shifted to higher frequency region and appears at 1640 cm^{-1}. This shift in ν(C—N) suggests the tendency of nitrogen coordinated to the metal ion.

Coordination of NO_3^- group[12] to the metal ion is indicated by the presence of a band at *ca.* 1020 cm^{-1}. Three additional bands of the perchlorate complexes at 1240, 1115 and 970 cm^{-1} can be attributed to ν_8, ν_6 and ν_1 vibrations of the coordianted ClO_4^- group respectively.[13]

At lower frequency region new band appears in the former complexes at 530–510 cm^{-1} and 440–425 cm^{-1} and are assigned to ν(M—O)[14] and ν(M—S)[15] respecively. In later complexes these bands appear at 480–460 cm^{-1} and 430–420 $cm^{-1}$and are assigned to ν(M—N)[16] and ν(M—S)[15] respectively.

In the light of infrared spectral data, it is evident that the former ligand is coordinated to metal ions through sulphur and carbonyl oxygen atom and the latter ligand coordinated to metal ions through sulphur and carbonyl nitrogen atom respectively. As the complexes are insoluble in water and common organic solvents, this seems to suggest a polymeric nature of the complexes, where in each ligand coordinates to two metal ions in *trans*-bi-bidentate form.

The electronic spectra of the Cu(II) complexes show the characteristic broad bands in the region 14,500–15,000 cm^{-1} and a strong band at 26,000 cm^{-1}. The broad band corresponds to $^2E_g \rightarrow {}^2T_{2g}$ transition in a nearly octahedral environment around the metal ion. The width and the symmetry of the band suggest tetragonal distortion and Jahn-Teller effect. The higher frequency band arises due to charge transfer. The magnetic moment values of the complexes are in the region 1.70–1.75 B.M. which is in agreement with the expected value for d^9 system with a distorted octahedral field.

The electronic spectra of the Ni(II) complexes show bands at *ca.* 9,000 cm^{-1}, 15,000 cm^{-1} and 25,500 cm^{-1} corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions respectively in an octahedral field. All these complexes are paramagnetic. The magnetic moment values lie in the range 2.56–2.70 B.M., which is expected for Ni(II) ion in an octahedral environment.

There are three bands in the electronic spectra of the Co(II) complexes. They are observed at *ca.* 17,000 cm^{-1}, 21,000 cm^{-1} and 28,000 cm^{-1} which may be assigned to the transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively and the third band is due to charge transfer. The magnetic moments of the complexes are *ca.* 5.0 B.M. which further suggest the high spin octahedral stereochemistry around Co(II) ion.

Fungicidal screening: The antifungal activity of the ligands and its metal complexes were tested against *Helminthosporium oryzae*, *Fusarium oxysporium* and *Aspergillus niger* by the method of Horsfall[17]. The evaluation was carried out at 1000 ppm in dioxane. The amount of germination or growth inhibition was determined after inoculation of the fungal spores onto Czapexdox agar-agar medium containing the test sample. The whole system was kept in an incubator for five days at 30 ± 1°C. The percentage inhibition was calculated as follows:

$$\% \text{ of inhibition} = \frac{100\,(P - Q)}{P}$$

where P = area of colony growth without test sample and Q = area of colony growth with test sample. When metal salts such as copper chloride, cobalt chloride are used as fungicides they cause damage to the level[18]. However, the coordiation compounds do little damage. Among the complexes being reported here, the copper(II) complexes possess the highest fungitoxicity. The fungitoxicity of the complexes has been attributed to the presence of the N—C=S moiety[19].

REFERENCES

1. H.G. Petering, H.H. Buskirk, J.A. Crim and G.J. Van Giessen, *Pharmacologist*, **5**, 273 (1963).
2. H.G. Petering, N.H. Buskirk and F.P. Kupiecki, *Fed. Proc. Fed. Amer. Soc. Exp. Biol.*, **21**, 1304 (1965).
3. J.A. Crim and H.G. Petering, *Cancer Res.*, **27**, 1278 (1967).
4. H.G. Petering and G.J. Van Giessen, The Biochemistry of Copper, Academic Press, New York, p. 197 (1966).
5. E.C. Horning, Organic Synthesis, Collective Vol. III, John Wiley, New York, p. 735 (1967).
6. A.I. Vogel, A Text Book of Quantitative Organic Analysis, ELBS and Longman, London, p. 462 (1968).
7. D.S. Mahadevappa and A.S. Anandamurty, *Aust. J. Chem.*, **7**, 25 (1972).
8. J.R. Dyre, Application of Absorption Spectroscopy of Organic Compounds, 3rd Edn., Prentice-Hall of India Ltd., New Delhi, p. 38 (1974).
9. L.J. Bellamy, Advances in Infared Group Frequencies, Methuen and Co., p. 117 (1968).
10. R. Rivest and S.C. Jain, J. Inorg. Nucl. Chem., **29**, 2787 (1967).
11. A. Yamaguchi, R.B. Penland, S. Mizushima, T.S. Lane, T.J. Curran and J.V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).
12. N.C. Rai and B. Sahoo, *J. Indian Chem. Soc.*, **53**, 636 (1976).
13. B.J. Hathaway and A.E. Underhil, *J. Chem. Soc.*, 2053, 3091 (1961).
14. J.Z. Karwecka and L. Pajdowaski, *Pol. J. Chem.*, **52**, 2053 (1978).
15. R.G. Gadag and M.R. Gajendragad, *Indian J. Chem.*, **16A**, 703 (1978).
16. S.N. Choube, J.P. Srivastava and L.K. Mishra, *Inorg. Chem. Acta.*, **23**, 1 (1977).
17. J.G. Horsfall, *Bot. Rev.*, **11**, 357 (1945).
18. J.C. Bailar, H.J. Eneleus, R. Nyholm and A.F. Trotman, Comprehensive Inorganic Chemistry, Vol. 3, Pergamon Press, New York, p. 3.
19. K.C. Satpathy, H.P. Mishra and R. Mishra, *J. Inorg. Nucl. Chem.*, **43**, 276 (1981).

(*Received*: 18 August 1998; *Accepted*: 30 January 1999) AJC-1684