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Coordination Behaviour of Some Aryl and Thiazolyl Hydrazones towards Dioxomolybdenum(VI)

A.K. SRIVASTAVA* and A.K. SINGH†
Department of Chemistry
B.R. Ambedkar Bihar University, Muzaffarpur-842 001, India

Aryl and thiazolyl hydrazones were synthesised by coupling reaction of diazotised solution of aniline, *o*-toluidine, 2-aminobenzothiazole and its methyl derivative with acetoacetanilide. These compounds were used as ligands and their dioxomolybdenum(VI) complexes were synthesised. On the basis of elemental analysis their compositions were proposed as $MoO_2L \cdot H_2O$, where L = thiazolylhydrazone and $MoO_2L \cdot 2H_2O$, where L = arylhydrazones. All the complexes were found to be diamagnetic and non-electrolytic in nature. The IR spectral studies revealed that after enolisation and subsequent deprotonation the thiazolyl hydrazones behaved as NOS donor dinegative ligand whereas aryl hydarazones behaved as NO donor dinegative ligands towards MoO_2^{2+} ion. All the complexes were *cis*-dioxo complexes. Pseudo octahedral geometry was tentatively proposed for all the synthesised complexes.

Key words: **Aryl, benzothiazolyl, hydrazones, dioxomolybdenum(VI), infrared.**

INTRODUCTION

Molybdenum is an essential micronutrient for microorganisms, plants and animals. The search for model systems of molybdenum site in enzymes has led to an increasing interest in the coordination chemistry of this element[1]. Hydrazone derivatives containing additional donor sites such as >C═O, heterocyclic nitrogen and sulphur systems have interesting ligational features and several earlier workers have reported a large number of coordination compounds with such ligands[2–4]. However, survey of literature revealed that no attempts have been made to investigate coordination behaviour of hydrazone ligands containing thiazole moiety towards molybdenum.

In continuation of our earlier work with such ligands[5, 6], we report here the synthesis of some hydrazones derived by the coupling reaction of diazotised solution of benzothiazole, 5-methyl-2-aminobenzothiazole aniline and *o*-toluidine with acetoacetanilide. The coordination behaviour of ligands towards molybdenum(VI) has also been described.

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†Government Postgraduate College, Dhamtari (Chattisgarh), India.

EXPERIMENTAL

All the chemicals and solvents were of AR grade and purified by standard methods. The infrared spectra using Perkin-Elmer spectrophotometer, UV spectra by Perkin-Elmer Lambda-15 UV-vis spectrophotometer and elemental analysis were recorded at CDRI, Lucknow.

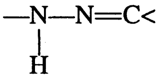
The ligands were synthesised by the methods described in literature[7] in similar compounds.

Preparation of Ligands: Aniline, *o*-toluidine, 2-aminobenzothiazole and 2-amino-5-methyl benzothiazole (0.1 mol) were dissolved in concentrated hydrochloric acid (25 mL) cooled to 0°C and a solution of sodium nitrite (7 g) in water (17 mL) was added dropwise to it maintaining the temperature between 0–5°C. The filtered diazotised solution was added dropwise to a stirred solution of acetoacetanilide (0.1 mL) in acetone (100 mL) to which a solution of sodium acetate (36 g) in water (100 mL) had been added. The solution was stirred for 2 h. The yellow crystalline product was filtered, washed with water and dried. The crude product was recrystallized by glacial acetic acid and purity was ascertained by TLC. The structures of various ligands are shown in Fig. 1.

Preparation of Complexes with Molybdenum(VI): The ligands (0.1 mol) were shaken with saturated aqueous sodium bicarbonate (10 mL) and the resulting solution was added to a solution of ammonium molybdate (0.1 mol) dissolved in 20 mL dilute sulphuric acid (0.1 M). After the vigorous reaction ceased, the resulting solution was refluxed for 2.5 h and the brownish crystalline product obtained on cooling was filtered off, washed with ethanol and dried in vacuum.

RESULTS AND DISCUSSION

The analytical data of the coupling product have been summarised in Table-1. All the ligands were displaying broad electronic spectral bands around 235 nm and 368 nm characterising the $>C{=}O$ and $-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\mathrm{N}{=}\mathrm{C}<$ chromophoric group.



$$-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\mathrm{N}{=}\mathrm{C}<$$

One additional band in ligand H_2btaa and H_2mbtaa at around 204 nm may be assigned due to thiazole moiety.

TABLE-1
CHARACTERISTIC DATA OF LIGAND COMPOUNDS

Ligands (colour)	% of N, found (calcd.)	m.p. (°C)	Yield (%)	IR spectral band with tentative assignment (cm^{-1})				UV recorded band (nm)
				ν(N–H)	ν(C=O)	ν(C=N)	ν(C–S–C)	
(H_2btaa) (Yellow)	16.7 (16.5)	160	80	3175 b, w	1675 s 1630 m	1580 s 1530 s	873 m	204, 234, 367
(H_2mbtaa) (Deep yellow)	15.9 (16.0)	165	75	3170 b, w	1672 s 1625 m	1585 s 1535 s	873 m	203, 236, 368
(H_2anaa) (Light yellow)	14.8 (14.9)	125	70	3081 b, m	1670 s 1598 s	1490 s		235, 369
(H_2tnaa) (Light yellow)	14.3 (14.2)	135	65	3080 b, m	1665 s 1600 s	1480 s		235, 369

The infrared spectral band with the tentative assignments (Table-1) suggests the following hydrazone structure to the ligands[8].

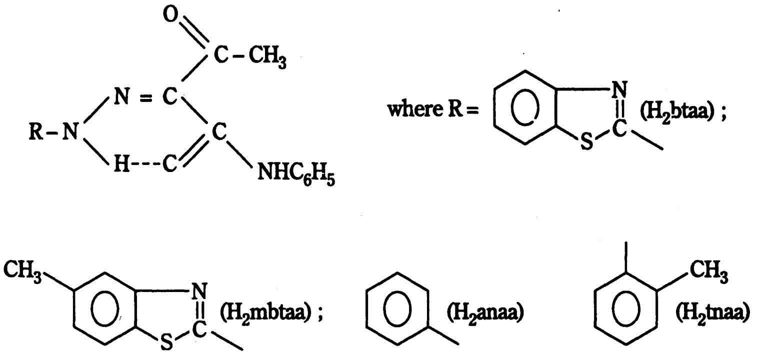


Fig. 1. Structure of different ligands

All the molybdenum complexes isolated were found to be insoluble in common organic solvents, non-electrolytes in DMF and diamagnetic in nature. The characterisation data for complexes have been summarised in Table-2.

TABLE-2

Complexes (colour)	% analysis, found (calcd.) N	% analysis, found (calcd.) Mo	m.p. (°C)	Yield (%)	IR spectral bandS (in cm^{-1}) ν(H_2O)	ν(C=O)	ν(C=N)	ν(C–S–C)
MoO_2(btaa)·H_2O	11.7	19.7	210 d	63	3553 b	1628 m	1580 s	835
(Grey)	(11.6)	(19.9)			3440 b		1530 s	
MoO_2(mbtaa)·H_2O	11.4	19.5	215 d	70	3550 b	1625 m	1585 s	834
(Dim green)	(11.2)	(19.3)			3442 b		1535 s	
MoO_2(anaa)·$2H_2O$	9.6	21.8	220 d	73	3558 b	1598 s	1490 s	–
(Parrot green)	(9.4)	(21.6)			3447 b			
MoO_2(tnaa)·$2H_2O$	9.0	20.9	240 d	72	3556 b	1596 s	1480 s	–
(Green)	(9.1)	(21.0)					3448 b	

The complexes were found to have composition $MoO_2L{\cdot}2H_2O$ (where H_2L = H_2anaa and H_2tnaa) and $MoO_2L.2H_2O$ (where H_2L = H_2btaa and H_2mbtaa) and are diamagnetic in nature.

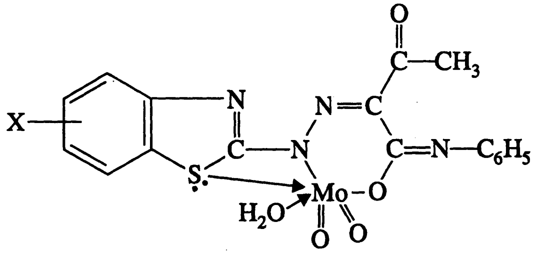
In the electronic spectra of complexes, all ligand bands were found to be shifted to slightly higher region with one additional band around 390–400 nm. It was inferred that no major structural change is taking place during complexation. The band around 390–400 nm is assigned as CT band[9].

The appearance of new and strong bands in all complexes around 910 cm^{-1} is due to the presence of O═Mo═O species in these complexes[10]. The broad hump in the region 3558–3553 cm^{-1} and 3447–3440 cm^{-1} in all complexes are suggestive of hydrated complexes. The loss of water molecule above 180°C suggests that water molecules are inside the coordination sphere. In all complexes the disappearance of band around 3175–3080 cm^{-1} and around 1670 cm^{-1} clearly suggests enolisation of a carbonyl group and deprotonation of both protons (N—H and O—H). The peaks around 1585– 1580 cm^{-1} and 1535–1490 cm^{-1} of ligands remain intact which suggests that one carbonyl group azomethine nitrogen and cyclic nitrogen of thiazole moiety is not involved in coordination.

One additional feature in IR spectra of complexes $MoO_2(btaa)\cdot H_2O$ and $MoO_2(mbtaa)\cdot H_2O$ is observed, *i.e.*, shifting of (C—S—C) peak of ligand from 873 cm^{-1} to 835 cm^{-1}. We conclude that thiazolyl sulphur in these ligands were also involved in coordination.

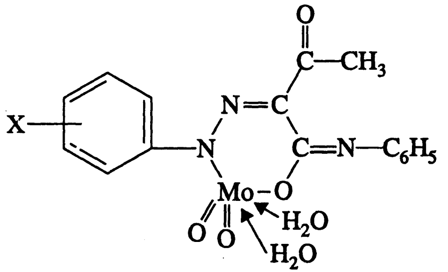
Thus it can be concluded on the basis of above findings that the ligand H_2btaa and H_2mbtaa behaved as dianionic ONS donors and H_2anaa and H_2tnaa as dianionic ON donor towards dioxomolybdenum(VI) cation. A tentative structure of the complexes may be proposed on this basis as

(1) $MoO_2L\cdot H_2O$ where H_2L=H_2 btaa and H_2 mbtaa



where X=H or 5-methyl

(2) $MoO_2L\cdot 2H_2O$ where H_2L=H_2 anaa and H_2 tnaa



where X=H or 2-methyl

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REFERENCES

1. M.J. Barker, M.P. Coughlam and L.M. Siegel, *Biochemistry*, **21**, 3561 (1982).
2. R.L. Dutta and M.M. Hossain, *J. Sci. Ind. Res.*, **44**, 635 (1985).
3. R.N. Goyal, A. Monocha, Anita Agrawal and V.R. Singh, *Bull. Soc. Chem. Fr.*, **1**, 58 (1985); *Chem. Abstr.*, **103**, 78159 (1985).
4. A.K. Srivastava, Ph.D. Thesis, Bihar University (1989).
5. N. Prasad, A. Sahay and A.K. Srivastava, *Proc. Nat. Acad. Sci. (India)*, **60**, 147 (1990).
6. N. Prasad, A.K. Srivastava, and A. Sahai, *Asian J. Chem.*, **3**, 281 (1991).
7. R.N. Goyal, Rajeev Jain and Sudha Tyagi, *J. Indian Chem. Soc.*, **58**, 504 (1981).
8. D. Prasad, N. Prasad, R.M. Prasad, R.J. Ferrier and S.M. Milligate, *J. Chem. Soc., Perkin Trans.*, **1**, 1397 (1984).
9. F.N. Moore and R.E. Rice, *Inorg. Chem.*, **7**, 2510 (1968).
10. P.C.H. Mitchell, *Quart. Rev.*, 103 (1966).

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