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Synthesis, Spectral and Antimicrobial Studies of Some Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes of a Schiff Base Derived from 1-Phenyl-2,3-dimethyl-4-amino-5-pyrazolone

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Some novel oxomolybdenum(V) complexes of general formula [MoO(TAAP)XCl_2] and dioxomolybdenum(VI) complexes of general formula [MoO_2(TAAP)XCl] (X = Cl, NO_3, NCS or ClO_4 and TAAP-1-phenyl-2,3,-dimethyl-4-(N-thienylidene)-5-pyrazolone) have been synthesized and characterized by elemental analysis, IR, UV, ESR and NMR spectral studies. The thermal behaviour of the complex [MoO_2(TAAP)NCSCl] has also been examined. The ligand and its few metal complexes were screened for their antibacterial activities against gram positive and gram negative bacteria and also screened for their antifungal activities. The molar conductance values of the complexes indicate that the complexes are non-electrolytes. The X-ray powder diffraction pattern of the complex [MoO_2(TAAP)(NCS)Cl] has been examined and found to be orthorhombic with the unit cell dimensions such as a = 24.35 Å, b = 10.89 Å and c = 9.94 Å. The X-band ESR spectra indicate that the pentavalent Mo in the complexes [MoO(TAAP)Cl_3], [MoO(TAAP)$NCSCl_2$] and [MoO(TAAP)ClO_4Cl_2] is monomeric in nature.

Key Words: Mo(V), Mo(VI), 1-Phenyl-2,3-dimethyl-4-amino-5-pyrazolone, Thiophene-2-aldehyde.

INTRODUCTION

Molybdenum complexes with organic ligands are the compounds of great theoretical and practical interest, especially valuable as model systems for biochemical processes. However, such attempts enrich the coordination chemistry of molybdenum in its higher oxidation state. A variety of chemical reactions are reported to be catalyzed by coordination compounds of molybdenum. It is an essential micronutrient for micro organisms, plants and animals[1].

In view of the importance of oxomolybdenum (V) and dioxomolybdenum(VI), we have isolated and characterized some new complexes of a multidentate ligand 1-phenyl 2,3-dimethyl 4-(N-thienylidene)-5-pyrazolone (TAAP) derived from biologically active molecule, 4-aminoantipyrine. TAAP is a bidentate neutral ligand.

EXPERIMENTAL

4-Aminoantipyrine (Fluka, Switzerland), $MoCl_5$ (Acros organics, Belgium) and Thiophene-2-aldehyde (Acros organics, Belgium) were used as such. All other chemicals were of BDH AR grade.

Preparation of the ligand TAAP: Thiophene-2-aldehyde and 4-aminoantipyrine were dissolved in methanol and refluxed for 15 min on a water bath. The reaction mixture was stirred well, the yellow crystals were filtered, washed and recrystallized from hot methanol (Fig. 1).

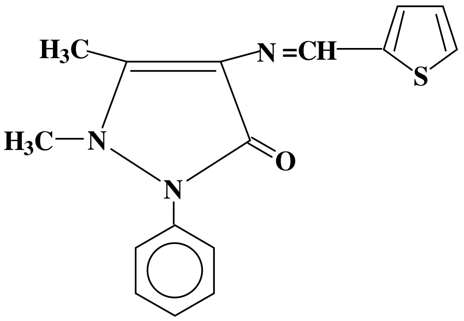


Fig. 1. 1-Phenyl-2,3-dimethyl-4-(N-thienylidene)-5-pyrazolone (TAAP)

Preparation of oxomolybdenum(V) complexes: A methanolic solution of $MoCl_5$ (2 mmol) was mixed with a hot methanolic solution of the ligand (2 mmol). It was then refluxed for *ca.* 5 h. The reaction mixture was concentrated, the solid separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

The following method[2] was adopted for the preparation of other oxomolybdenum(V) complexes.

Methanolic solutions of $MoCl_5$ (2 mmol), containing 2-3 drops of $HClO_4$/0.5 g of $LiNO_3$/0.5 g of NH_4NCS as the case may be were mixed with hot methanolic solution of ligand (2 mmol) and refluxed for *ca.* 5 h. The reaction mixture was concentrated, the complex separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

Preparation of dioxo molybdenum(VI) complexes: MoO_3 (2 mmol) was dissolved in conc. HCl. This solution was added dropwise with stirring to a hot methanolic solution of the ligand (2 mmol). It was then refluxed for *ca.* 5 h. The reaction mixture was concentrated, the complex separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

The following general method[2] was adopted for the preparation of other dioxomolybdenum(VI) complexes.

MoO_3 (2 mmol) was dissolved in conc. HCl. To this, added 2-3 drops of $HClO_4$/0.5 g of $LiNO_3$/0.5 g of NH_4NCS. This solution was added dropwise with stirring to a hot methanolic solution of the ligand (2 mmol) and refluxed for *ca.* 5 h. The reaction mixture was concentrated, the complex separated was filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

Metal and halide in the complexes were estimated by standard methods[3]. Perchlorate was estimated by Kurz's method[4]. Elemental analysis (C, H, N and S) of complexes were carried out at RSIC, CDRI, Lucknow. The IR spectra of the ligand and complexes were recorded in the region 4000-400 cm^{-1} on a Jasco FT-IR 430 spectrophotometer using KBr pellets. ^1H NMR spectra of the ligands were recorded in $CDCl_3$ on a 300 MHz FT NMR instrument using TMS as reference. X-ray powder diffraction pattern of the complexes were recorded using Philips X-ray PW 1710 diffractometer. The conductances of the complexes in $C_6H_5NO_2$, CH_3OH and CH_3CN were measured at 300 ± 2 K using an Elico conductivity bridge type CM 82T with a dip type cell (ec-03) fitted with platinum electrodes (cell constant 0.94 cm^{-1}).

RESULTS AND DISCUSSION

All the complexes are non-hygroscopic solids, soluble in CH_3OH, $C_6H_5NO_2$ and CH_3CN and sparingly soluble in other common organic solvents.

The analytical data of the complexes (Table-1) correspond to the composition [MoO(TAAP)XCl_2] for Mo(V) complexes and [MoO_2(TAAP)XCl] for Mo(VI) complexes. (TAAP = neutral ligand and X = Cl, NO_3, NCS or ClO_4). The molar conductances show that all the complexes are non-electrolytes.

Infrared spectra

In the IR spectrum, the ν(C=O) observed at 1642 cm^{-1} in the ligand spectra are shifted to 1602 cm^{-1} in the spectra of the complexes showing the participation of the C=O group in coordination. The ligand shows strong band in the region 1600 cm^{-1} assignable to ν(C=N) vibrational mode. The band due to ν(C=N) of the ligand undergoes a negative shift by *ca.* 20-40 cm^{-1} in the spectra of the complexes. This clearly indicates the coordination of azomethine nitrogen to metal atom. The ligand, TAAP exhibits characteristic bands corresponding to the in plane and out of plane deformation of 2-substituted thiophene at 754 and 563 cm^{-1}, respectively[5,6] remain unchanged in the spectra of the complexes also. This reveals the non-coordination of thiophene ring sulphur atom to metal atom[7,8]. Thus the ligand TAAP behaves as neutral bidentate chelating agent in these complexes.

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA OF MOLYBDENUM COMPLEXES

Complex	Elemental analysis: Found (Calcd.) %					Molar conductance (Ω^{-1} cm^2 mol^{-1})					
	C	H	N	S	Mo	$C_6H_5NO_2$ conc. × 10^{-3}	Cond.	CH_3CN conc. × 10^{-3}	Cond.	CH_3OH conc. × 10^{-3}	Cond.
[MoO(TAAP)Cl_3]	37.30 (37.26)	2.95 (2.91)	8.18 (8.15)	6.25 (6.21)	18.65 (18.62)	0.99	4.70	1.00	11.20	1.00	7.90
[MoO(TAAP)$NCSCl_2$]	37.90 (37.93)	2.85 (2.79)	10.44 (10.41)	11.88 (11.90)	17.88 (17.84)	1.10	5.90	1.00	31.10	1.10	18.50
[MoO(TAAP) NO_3Cl_2]	35.47 (35.41)	2.79 (2.76)	10.30 (10.33)	5.85 (5.90)	18.30 (18.36)	1.10	7.30	1.00	50.80	1.10	9.60
[MoO(TAAP)ClO_4Cl_2]	33.18 (33.14)	2.63 (2.59)	7.20 (7.25)	5.56 (5.52)	16.50 (16.56)	0.99	7.80	1.00	8.50	0.93	8.30
[MoO_2(TAAP)Cl_2]	38.75 (38.71)	2.5 (3.0)	8.40 (8.47)	6.40 (6.45)	19.30 (19.35)	1.10	2.04	0.98	7.48	1.00	6.66
[MoO_2(TAAP)NCSCl]	39.40 (39.35)	2.92 (2.89)	10.72 (10.80)	12.39 (12.34)	18.45 (18.50)	1.10	2.24	1.00	34.80	1.00	24.50
[MoO_2(TAAP)NO_3Cl]	36.70 (36.75)	2.80 (2.87)	10.76 (10.72)	6.10 (6.13)	18.32 (18.36)	1.00	2.81	1.00	53.60	1.00	7.80
[MoO_2(TAAP)ClO_4Cl]	34.25 (34.29)	2.62 (2.68)	7.55 (7.50)	5.78 (5.72)	17.05 (17.13)	1.00	2.25	0.94	11.80	1.00	15.20

A very strong band at 1059 cm^{-1} and a medium intensity band at 617 cm^{-1} observed in the spectrum of the perchlorate complex of molybdenum(V) are assigned to ν_3 and ν_4, respectively. In the spectrum of [MoO_2(TAAP) (ClO_4)Cl], two bands (split bands) observed at 1110 and 1029 cm^{-1} assigned to ν_4 and ν_1 and another set of split bands 638 and 625 cm^{-1} assigned to ν_3 and ν_5 vibrations are characteristic of monodentately co-ordinated perchlorate group. This is supported by the molar conductance data[8] (Table-1). The N co-ordinated nature[9] of the thiocyanate group is indicated by ν(C-N) (2056), ν(C-S) (798) and δ(NCS) (500 cm^{-1}). The IR spectra of the nitrate complexes are suggestive of monodentately co-ordinated nitrate groups[10] (ν_4 1500, ν_1 1379 cm^{-1}).

A very strong band found at 950 cm^{-1} in the spectra of Mo(V) complexes corresponds to Mo=O stretching frequency. The strong bands exhibited by the dioxomolybdenum(VI) complexes in the region 950-970 and 910 cm^{-1} are attributed to ν_{sym}(O=Mo=O and ν_{sym}(O=Mo=O), respectively of *cis*-MoO_2 configuration due to the maximum utilization of the available dπ orbitals for bonding with the oxo groups[11]. The Mo-N stretching frequency (Mo-N) lies 480 cm^{-1} in the complexes. Medium to weak intensity bands occurring 420-450 cm^{-1} are attributed to ν(Mo-O) in the complexes[12].

Electronic spectra: The electronic spectral bands of oxomolybdenum (V) complexes in methanol together with the tentative assignments are discussed[13]. The Mo(V) complexes usually exhibit three distinct absorption bands in the ligand field region at *ca.* 13500-14500, 19000-22000 and 22500-26000 cm^{-1}, assignable to the transitions $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$); $^2B_2 \rightarrow {}^2A$, ($d_{xy} \rightarrow d_{x^2-y^2}$) and $^2B_2 \rightarrow {}^2A_2$, ($d_{xy} \rightarrow d_{z^2}$). Usually, the third band is obscured by the more intense charge transfer transition O(π) → d(Mo) involving the excitation of an electron from the highest filled bonding M-O (associated mainly with oxygen) to the *d*-orbitals of molybdenum. All the present Mo(V) complexes show bands in the region 13698-14925 (Weak broad), 19608-20000 and 25000 cm^{-1}. The electronic spectra thus indicate octahedral environment for all the complexes and are in conformity with the Ballhausen-Gray scheme for an octahedral geometry[13]. No bands are observed below 10000 cm^{-1} and hence the possibility of a tetrahedral structure can be ruled out. The complexes can be best considered as octahedral with strong tetragonal distortion (C_{4v} symmetry), resulting from the Mo=O multiple bond.

^{1}H NMR spectra: In the ^{1}H NMR spectrum of the ligand TAAP, the signal of > C-CH_3 group of pyrazolone ring appears as a sharp singlet (3H) in the region δ 2.21-2.42. The N-CH_3 signal is observed as another singlet in the region δ 3.10-3.33. The aromatic protons of the compound appear as multiplet in the region δ 7.03-7.45. A detailed assignment of the aromatic proton signals are not attempted. On analyzing the spectra of the complex [MoO_2(TAAP)NO_3Cl], no appreciable change of signals observed. IR spectral data are also in confirmity with these observations.

ESR spectra: The X-band ESR spectra of four complexes such as [MoO(TAAP)Cl_3], [MoO(TAAP)NCSCl_2], [MoO(TAAP)NO_3Cl_2] and [MoO(TAAP)ClO_4Cl_2] were recorded in polycrystalline form at room temperature, exhibited a single line only. The ESR parameters calculated are given in Table-2. The g_{av} values indicate that the pentavalent Mo in the complexes are monomeric[14].

TABLE-2
ESR SPECTRAL DATA OF THE COMPLEXES

Complex	$g_{\parallel}$	$g_{\perp r}$	g_{av}
[MoO(TAAP)Cl_3]	1.9829	1.9234	1.9432
[MoO(TAAP)NCSCl_2]	1.9829	1.8726	1.9094
[MoO(TAAP)NO_3Cl_2]	1.9799	1.9044	1.9094
[MoO(TAAP)ClO_4Cl_2]	1.9859	1.9125	1.9370

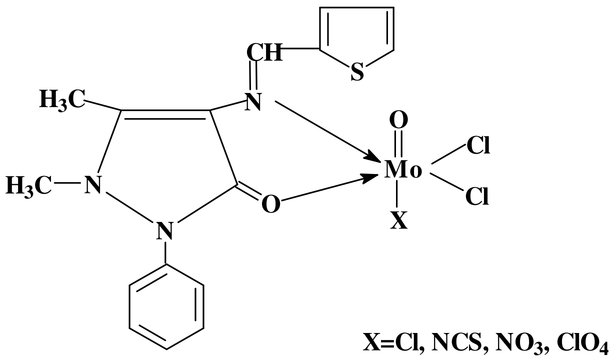
Thermal studies: Thermogravimetric curves of the complex [MoO_2(TAAP)NCSCl] was recorded in the temperature range from room temperature to 1000°C. The complex shows first a weight loss of 57.28 % around 245°C. This corresponds to the elimination of ligand molecule. The second weight loss of 6.85 % at 490°C was observed corresponding to the loss of chlorine atom. The third weight loss of 4.35 % at 551°C was observed corresponding to the loss of thiocyanate group. The residual mass is about 27.76 % which indicates that the decomposition[15] product is MoO_3.

X-ray diffraction studies: The complex [MoO_2(TAAP) (NCS)Cl] was found to be orthorhombic by X-ray powder diffraction method and was indexed using Hesse and Lipson's procedure[16,17]. The lattice constants are A = 0.001, B = 0.005 and C = 0.006 and hence the unit cell dimensions a, b and c for the complex was found to be 24.35, 10.89, 9.94 Å, respectively.

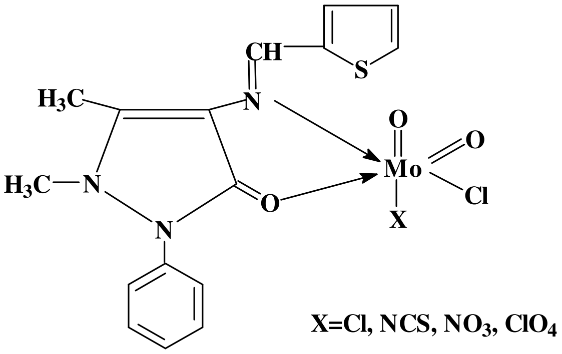
Biological activities: The ligand TAAP and the complexes [MoO(TAAP)(NCS)Cl_2] and [MoO_2(TAAP)(NCS)Cl] were screened for their possible antibacterial activities[18] against the gram positive bacteria *Staphylococcous aureus* ATCC 25923 and gram negative bacteria *Escherichia coli* ATCC 25922 at concentrations 5, 10, 20, 40 and 80 µg/disc tested. The complex [MoO_2(TAAP)(NCS)Cl] exhibited antimicrobial activity against *S. aureus* ATCC 25923 at all concentrations tested. But TAAP and [MoO(TAAP)(NCS)Cl_2] did not show any antibacterial activity against both gram positive and gram negative bacteria at all concentrations tested.

TABLE -3
BACTERICIDAL SCREENING DATA OF THE COMPLEX
[MoO_2(TAAP)NCSCl]
Diameter of disc (for test and control samples) 6 mm

Sample	Zone of inhibition			
	E. coli ATCC 25922		*S. aureus* ATCC 25923	
[MoO_2(TAAP)NCS Cl]	5 µg/disc	Nil	5 µg/disc	10 mm
	10 µg/disc	Nil	10 µg/disc	10 mm
	20 µg/disc	Nil	20 µg/disc	10 mm
	40 µg/disc	Nil	40 µg/disc	10 mm
	80 µg/disc	Nil	80 µg/disc	10 mm
Gentamicin	10 µg/disc	19 mm	10 µg/disc	24 mm
Negative control	–	Nil	–	Nil



[MoO(TAAP) X Cl_2]



[MoO_2(TAAP) X Cl]

Fig. 2. Suggested structure of the metal complexes

The ligand and the complexes [MoO_2(TAAP)NCSCl] and [MoO(TAAP)NO_3Cl_2] were screened for their antifungal activities using poisoned food technique[19]. The ligand and the complexes were found to be active against Fusarium oxysporum species which causes wilt in tomato. The growth of the colony in control sets was compared with that of the various treatments and percentage inhibition was calculated.

$$\% \text{ inhibition} = \frac{\text{Growth in control - Growth in sample} \times 100}{\text{Growth in control}}$$

Results showed that the complexes exhibited significant antifungal profile. On the basis of the above evidences, a distorted octahedral geometry is suggested for the complexes (Fig. 2).

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