Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 109, No. 1, February 1997, pp. 7–13.

Synthesis and characterisation of molybdenum (V) and (VI) complexes of 2, 6-diformyl-*p*-cresol-*bis*[4-(X-phenyl) thiosemicarbazone]

ULLAS N SHETTI, VIDYANAND K REVANKAR and VINAYAK B MAHALE*
Department of Chemistry, Karnatak University, Dharwad 580 003, India

MS received 30 May 1996; revised 2 November 1996

Abstract. Molybdenum (V) and (VI) complexes of novel ligand 2, 6-diformyl-*p*-cresol *bis* [4-(X-phenyl) thiosemicarbazone] (where X = -H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *p*-OCH_3 and *p*-Cl) are synthesised and characterised on the basis of elemental analyses and magnetic, IR, UV, EPR, and NMR spectral studies. The complexes have the composition [MoO_2LH] and [MoOClLH]. The Schiff bases behave as dibasic tetradentate SNON donor ligands.

Keywords. Molybdenum (V) and (VI) complexes; thiosemicarbazone.

1. Introduction

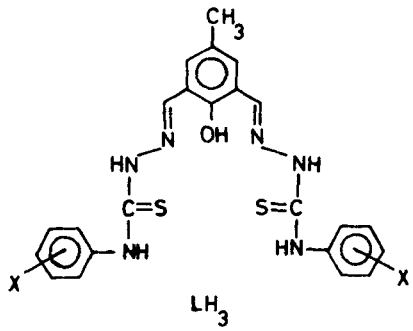
The chemistry of molybdenum has been receiving increasing attention (Marabella *et al* 1983; Topich and Lyon 1984; Berg and Holm 1985; Holm 1987, 1990; Cleland *et al* 1987; Purohit *et al* 1989; Craig *et al* 1989; Hinshaw *et al* 1989), much of which is due to increasing biochemical redox reactions associated with enzymes such as nitrogenase, aldehyde oxidase, xanthine dehydrogenase, nitrate reductase etc. Sulphur donors have assumed special importance in this respect because of their presence inside the coordination sphere of Mo in molybdoenzymes (Cramer *et al* 1979; Tullius *et al* 1979; Choudary 1985; Hinshaw *et al* 1989). Various dithio ligands (Bhattacharjee and Bhattacharyya 1993, 1995) have been utilised extensively to gain insight into the chemistry of molybdenum ligated to sulphur donor centres. Thiosemicarbazone, a versatile organic reagent, has remarkable chelating ability, and possesses a wide spectrum of biological activities like antibacterial and antitumour properties and also medicinal properties (Campbell 1975; Klayman *et al* 1979; Scovill *et al* 1982).

The significant role played by molybdenum in biological systems and the pharmacological potential of thiosemicarbazone was the impetus for us to synthesise and characterise molybdenum (V) and (VI) complexes of the newly synthesised thiosemicarbazones referred to in this paper, derived from 2, 6-diformyl-*p*-cresol and 4-(X-phenyl) thiosemicarbazide.

These thiosemicarbazones have three interesting features.

(1) The ligands contain SNONS donor sequences possessing five potential coordinating sites.
(2) The ligands can bind two metal ions leading to oxobridged binuclear complexes.

*For correspondence



X = -H – DPHTSH$_3$
= -*o*-CH$_3$ – DOTTSH$_3$
= -*m*-CH$_3$ – DMTTSH$_3$
= -*p*-CH$_3$ – DPTTSH$_3$
= -*p*-OCH$_3$ – DPATSH$_3$
= -*p*-Cl – DPCTSH$_3$

(3) The ligands can behave as monobasic, dibasic or tribasic moieties depending on reaction conditions and the nature of the metal ions.

2. Experimental

Aniline, substituted anilines and other chemicals used in the preparation were of reagent grade. Anilines were distilled or recrystallised prior to use. The preparation of 2, 6-diformyl-*p*-cresol was carried out according to the reported method (Denton and Suschitzky 1963) with slight modifications. The synthesis of 4-phenylthiosemicarbazide and substituted thiosemicarbazide is carried out according to the procedure reported elsewhere (Sen and Gupta 1962).

2.1 *Preparation of aryl thiosemicarbazones*

Aryl thiosemicarbazide (0·021 mol) in ethanol (100 ml) was treated with 2, 6-diformyl-*p*-cresol (0·01 mol) and the reaction mixture refluxed for 3–4 h. The yellow solid that separated was filtered, washed with ethanol (2–3 times) and dried. Yield: 90%.

2.2 *Preparation of [MoO_2LH] (for complexes (1)–(6))*

$MoO_2(acac)_2$ (0·001 mol) (Chen *et al* 1976) in ethanol (50 ml) was treated with thiosemicarbazone ligand, (0·001 mol) and the orange yellow mixture stirred for 6–7 h with a magnetic stirrer. The fine microcrystalline complex formed was separated out by filtration on a Gooch crucible, washed with ethanol and dried. Poor solubility of the complexes in common organic solvents did not permit their recrystallisation. However, complexes were purified in a soxhlet extractor using ethanol as solvent. Yield: 80%.

2.3 *Preparation of [MoOLHCl] (for complex (7)–(11))*

The filtrate obtained by dissolving $(NH_4)_2$ [$MoOCl_5$] (0·002 mol) in absolute ethanol (40 ml) was added dropwise to the solution of ligand (0·002 mol) in ethanol (20 ml). The mixture was stirred with a magnetic stirrer for 7–8 h in an N_2 atmosphere. The brown solid that separated was filtered through a Gooch crucible (G3), washed with ethanol and purified in a soxhlet extractor using ethanol as solvent. Yield: 85%.

3. Analysis and physicochemical measurements

The elemental analyses of complexes for metal, nitrogen, sulphur and chloride were carried out by standard methods (Vogel 1969). Infrared spectra of the ligands and complexes in KBr were recorded using a Perkin–Elmer 783 spectrometer in

4000–400 cm^{-1} region. Electronic spectra of the ligands and the complexes in DMF solutions were recorded using a Hitachi 150–20 spectrophotometer in the 900–200 nm range. Electron spin resonance spectra of a few complexes in polycrystalline state were scanned on a Varian E-4 X-band EPR spectrometer, at room temperature (RT) with DPPH as '*g*' marker. ^1H NMR spectra were recorded in d_6 DMSO solvent on a Varian VXR 300S spectrometer. Magnetic susceptibility measurements of the complexes were carried out at room temperature, by the Gouy method using Hg $[Co(SCN)_4]$ as calibrant.

4. Results and discussion

All the complexes of molybdenum (VI) and (V) are insoluble in water, sparingly soluble in methanol and ethanol but soluble in DMF and DMSO. Elemental analyses data are shown in table 1. Molybdenum (VI) complexes are orange, while molybdenum (V) complexes are brown in colour. Reactions with various metal to ligand ratios resulted in the formation of a 1:1 complex only. Molar conductivities in DMF solution (8–16 mho cm^2 mol^{-1}) suggests that the complexes are nonelectrolytes.

Complexes (1) to (6) are diamagnetic as expected for Mo(VI), d^0 system. Complexes (7) to (11) have shown magnetic moment 1·58 to 1·71 BM, which is slightly less than expected (1·68–1·78) for magnetically dilute Mo(V) complexes with d^1 configuration (Steifel 1977).

Table 1. Elemental analyses and magnetic data of complexes.

Complex	Elemental analyses (%), found (calc.)				Magnetic moment μ_{eff} (BM)
	Mo	N	S	Cl	
$[MoO_2$ (DPHTSH)], 1	16·21 (16·33)	14·14 (14·29)	10·64 (10·88)		Diamag
$[MoO_2$ (DOTTSH)], 2	15·49 (15·58)	13·50 (13·64)	10·20 (10·39)		Diamag
$[MoO_2$ (DMTTSH)], 3	15·40 (15·58)	13·81 (13·64)	10·55 (10·39)		Diamag
$[MoO_2$ (DPTTSH)], 4	15·42 (15·48)	13·69 (13·64)	10·23 (10·39)		Diamag
$[MoO_2$ (DPATSH)], 5	14·78 (14·81)	12·89 (12·96)	9·76 (9·88)		Diamag
$[MoO_2$ (DPCTSH)], 6	14·74 (14·61)	12·85 (12·79)	9·83 (9·74)		Diamag
[MoOCl (DPHTSH)], 7	15·69 (15·80)	13·69 (13·83)	10·42 (10·53)	5·96 (5·84)	1·71
[MoOCl (DMTTSH)], 8	15·24 (15·11)	13·41 (13·22)	10·15 (10·07)	5·65 (5·59)	1·62
[MoOCl (DPTTSH)], 9	15·20 (15·11)	13·17 (13·22)	10·21 (10·07)	5·68 (5·59)	1·69
[MoOCl (DPATSH)], 10	14·49 (13·24)	12·43 (12·55)	9·42 (9·56)	5·39 (5·30)	1·58
[MoOCl (DPCTSH)], 11	14·10 (14·15)	12·45 (12·38)	9·59 (9·43)	5·32 (5·23)	1·65

Table 2. IR spectral data of complexes.

Complex	ν(C–H)		ν(C=H)	$\nu(MoO_2)$	
	(^{4}NH),	(^{2}N–H)		(sym)	(asym)
[MoO_2 (DPHTSH)], 1	3279	3131	1595	931	898
[MoO_2 (DOTTSH)], 2	3296	3156	1592	945	895
[MoO_2 (DMTTSH)], 3	3290	3135	1596	940	890
[MoO_2 (DPTTSH)], 4	3269	3146	1597	937	900
[MoO_2 (DPATSH)], 5	3280	3150	1590	950	910
[MoO_2 (DPCTSH)], 6	3260	3129	1596	943	900
[MoOCl (DPHTSH)], 7	3266	3150	1596	939	
[MoOCl (DMTTSH)], 8	3281	3148	1598	938	
[MoOCl (DPTTSH)], 9	3271	—	1594	940	
[MoOCl (DPATSH)], 10	3289	3145	1589	935	
[MoOCl (DPCTSH)], 11	3280	3170	1592	945	

4.1 *Infrared spectral studies*

Important IR bands with tentative assignments are presented in table 2.

In all the complexes, the band around 3130 cm^{-1} which was assigned to $\nu(^2N–H)$ in the ligand, decreases in intensity (nearly half) relative to $\nu(^4N–H)$ on complexation. This suggests that the ^{2}N–H proton has undergone deprotonation through enolisation on complexation. The lowering in intensity of this band suggests only one –NH group is deprotonated and not both. This evidence is further confirmed by NMR spectra. The ν(O–H) broad band around 2800–2600 cm^{-1} has disappeared in complexes suggesting deprotonation of phenolic oxygen on coordination to metal.

The sharp band at 1595–1602 cm^{-1} which was assigned to ν(C=N) has shifted to lower energy by 3–11 cm^{-1} suggesting coordination of both nitrogens to molybdenum. The band at around 860 cm^{-1} in the ligand which was assigned to ν(C=S) has lowered considerably in intensity, suggesting involvement of sulphur in coordination. However, the appearance of this band at lower energy could not be traced due to overlapping bands of ligand.

4.2 *Electronic spectra*

The spectral data are shown in table 3. The bands at 550 and 264 nm are common in ligands and complexes. In the complexes (1) to (6), shoulders or bands at 360 and 318 nm are assigned to ligand to metal charge-transfer transitions. No band is observed beyond 600 nm suggesting molybdenum in +6 oxidation state, which is also confirmed by the diamagnetic behaviour.

Complexes (7) to (9) show a broad band or shoulder around 650–680 nm, which is assigned to an $^2E \leftarrow {}^2B_2$ transition. Another band, expected at around 440–470 nm for $^2B_1 \leftarrow {}^2B_2$ transition, appears as a weak shoulder. These two bands are characteristic of monomeric molybdenum (V) species, a conclusion which is also supported by magnetic data and EPR spectra. The other bands at around 350 and 320 nm are assigned to ligand to metal charge-transfer transitions.

Table 3. Electronic and EPR spectral data of complexes.

Complex	Electronic spectral data	EPR parameters			
	λ_{max}(nm) (ε, $M^{-1}cm^{-1}$)	g	$g_\perp$	$g_\parallel$	g_{av}
$[MoO_2(DPHTSH)]$, 1	550(*sh*), 360(*sh*), 318, 264	No signal			
$[MoO_2(DOTTSH)]$, 2	373, 319, 264	No signal			
$[MoO_2(DMTTSH)]$, 3	550, 357, 318, 264	No signal			
$[MoO_2(DPTTSH)]$, 4	550, 358, 318, 264	—			
$[MoO_2(DPATSH)]$, 5	550, 372, 318, 264	—			
$[MoO_2(DPCTSH)]$, 6	545, 360(*sh*), 314, 264	—			
[MoOCl(DPHTSH)], 7	650(280), 450(4200)	1·94	1·97	1·92	1·95
[MoOCl(DMTTSH)], 8	660(385), 435(4600)				
[MoOCl(DPTTSH)], 9	680(190), 470(7800)	1·94	1·97	1·91	1·95
[MoOCl(DPATSH)], 10	675(415), 460(6200)	1·95	1.97	1·91	1·95
[MoOCl(DPCTSH)], 11	680(405), 440(4150)				

Table 4. ^{1}H NMR spectral data of ligand and complexes (in δ).

Compound	$-CH_3$	Aromatic protons	Azomethine proton	$-^4$NH (phenyl)	$-^2$NH (hydrazine)
$DPHTSH_3$	2·30	7·13–7·76	8·46	10·18	11·86
$[MoO_2(DPHTSH)]$	2·32	6·99–8·26	8·55	9·74	11·84
			8·76	10·08	11·77
$DPATSH_3$	2·29	6·92–7·75	8·44	10·07	11·77
$[MoO_2(DPATSH)]$	2·31	6·86–8·24	8·51	9·59	11·76
			8·67	9·87	

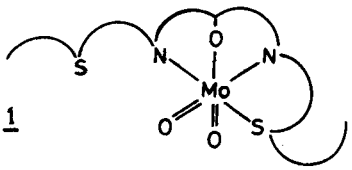
4.3 *Electron paramagnetic resonance spectral studies*

The complexes (1) to (3) are EPR silent. Complexes (7) and (9) exhibit signals characteristic of molybdenum (V) species (table 3). Interestingly, complex (10) shows a broad signal. The g values found (g = 1·94–1·95) are close to the values reported for other oxomolybdenum species.

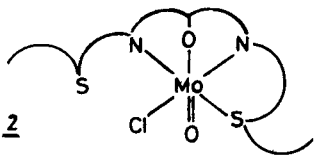
4.4 ^{1}*H NMR spectral studies*

The assignments of various signals in NMR spectra are indicated in table 4. Phenolic proton signals could not be observed in the 0–15ppm region studied. On D_2O exchange, both –NH signals disappear.

In complexes of $DPHTSH_3$ and $DPATSH_3$, the azomethine proton signals show downfield shift (8·51–8·77 ppm), suggesting coordination of azomethine nitrogens. Interestingly, the signal undergoes splitting with equal intensity. The phenyl –NH proton signal in



1



2

the complex has shifted upfield, and is split into two signals of equal intensity. Further, in complex (5) the $-OCH_3$ proton of the *p*-anisoyl moiety has also shown splitting. These splittings may be due to the dissymmetry caused by nonplanarity of the ligand on complexation (Yamanouchi and Yamada 1974). Further the hydrazine –NH signal has shifted upfield with decreased intensity (which corresponds to one proton). This suggests that only one part of thiosemicarbazone has undergone deprotonation through thioenolisation. Deuterium exchange of complexes shows disappearance of the –NH signal. Thus NMR spectra revealed the coordination of azomethine nitrogens and one thioketo sulphur to molybdenum (which is supplementary to IR) and also nonplanarity of ligand on complexation.

On the basis of elemental analyses, magnetic, IR, electronic, EPR, and NMR spectral studies, structures 1 and 2 are proposed for complexes (1)–(6) and (7)–(11) respectively.

Acknowledgements

The authors thank the Regional Sophisticated Instrumentation Centres at the Indian Institutes of Technology, Mumbai and Chennai for the spectral facilities. One of the authors (UNS) thanks the University Grants Commission, New Delhi for financial assistance.

References

Bhattacharjee S and Bhattacharyya R 1993 *J. Chem. Soc., Dalton Trans.* 1151
Bhattacharjee S and Bhattacharyya R 1995 *Proc. Indian Acad. Sci. (Chem. Sci.)* **107** 343
Berg J M and Holm R H 1985 *J. Am. Chem. Soc.* **107** 917
Chen G J J, McDonald J W and Newton W E 1976 *Inorg. Chem.* **15** 2612
Campbell M J M 1975 *Coord. Chem. Rev.* **15** 279
Choudary M 1985 *Inorg. Chem.* **24** 3011
Cleland W E Jr, Barnhart K M, Yamanouchi K, Collison D, Mabbs F E, Ortega R B and Enemark J H 1987 *Inorg. Chem.* **26** 1017
Cramer S P, Gray H B and Rajagopalan K V 1979 *J. Am. Chem Soc.* **101** 2772
Craig J A, Harlon E W, Snyder B S, Whitener M A and Holm R H 1989 *Inorg. Chem.* **28** 2082
Denton D A and Suschitzky 1963 *J. Chem. Soc.* 4741
Hinshaw C J, Peng G, Singh R, Spence J T, Enemark J H, Buch M, Kristofzski J, Merbs S L, Ortega R B and Wexler P A 1989 *Inorg. Chem.* **28** 4483
Holm R H 1987 *Chem. Rev.* **87** 1401
Holm R H 1990 *Coord. Chem. Rev.* **100** 183
Klayman D L, Bartosevich J F, Griffin T S, Mason C J and Scovill J P 1979 *J. Mednl. Chem.* **22** 853
Marabella C P, Enemark J H, Miller K F, Bruce A E, Pariyadath N, Corbin J L and Steifel E I 1983 *Inorg. Chem.* **22** 3456
Purohit S, Koley A P, Prasad L S, Manoharan P T and Ghosh S 1989 *Inorg. Chem.* **28** 3735

Scovill J P, Klayman D L and Franchino C F 1982 *J. Mednl. Chem.* **25** 1261
Sen A K and Gupta S K 1962 *J. Indian Chem. Soc.* **39** 628
Steifel E I 1977 *Prog. Inorg. Chem.* **22** 1
Topich J and J T Lyon 1984 *Inorg. Chem.* **23** 3202
Tullius T D, Kurtz M, Conradson S D and Hodgson K O 1979 *J. Am. Chem. Soc.* **101** 2776
Vogel A I 1969 *A text book of quantitative inorganic analysis* 3rd edn (London: ELBS, Longmans Green)
Yamanouchi K and Yamada S 1974 *Inorg. Chim. Acta* **9** 161