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Received for review October 17, 1977. Accepted March 24, 1978. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

NEW COMPOUNDS

Synthesis of *N*,*N'*-Diarylformamido-*N''*-arylcarbamides and -thiocarbamides and *N*-Benzoylformamido-*N'*-arylcarbamides and -thiocarbamides and Their Molybdenum(V) Chloride Complexes

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New dimeric complexes of molybdenum(V) chloride with *N*,*N'*-diarylformamido-*N''*-arylcarbamides and -thiocarbamides and *N*-benzoylformamido-*N'*-arylcarbamides and -thiocarbamides having a general formula $[MoCl_2L_2]Cl_3$ have been synthesized in chloroform solution (where L = a molecule of bidentate ligand). These complexes have been characterized on the basis of elemental analysis conductance in solution, magnetic susceptibility, and infrared spectral studies. The coordination, through sulfur and nitrogen in the case of *N*,*N'*-diarylformamido-*N''*-arylthiocarbamides and *N*-benzoylformamido-*N''*-arylthiocarbamides and through oxygen and nitrogn in the case of *N*,*N'*-diarylformamido-*N''*-arylcarbamides and *N*-benzoylformamido-*N'*-arylcarbamide, and octahedral configuration of these complexes have been proposed.

Introduction

The complex compounds of $MoCl_5$ with a number of primary, secondary, and tertiary amines were prepared by Edwards and Fowles (*4*) in benzene solution. The formation of Mo(V) and Mo(VI) complexes with 8-hydroxyquinoline-5-sulfonic acid has been reported by Spence and Peterson (*7*) and they have calculated the formation constants. Nitrogen donor ligands can produce Mo(IV) complexes with $MoCl_5$ but there are complexes where reduction does not occur. 2,4,6-Trimethylpyridine forms $MoCl_4(Me_3C_5H_2N_2)_2Cl$, for which the effective magnetic moment is 1.41 μ_B (*1*).

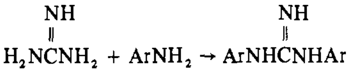
A careful survey of the literature revealed that no work has been done on the complex-forming ability of substituted formamido(N''-substituted)thiocarbamides and -carbamides. The present communication describes our studies on the synthesis of *N*,*N'*-(diaryl substituted)formamido-*N''*-arylcarbamides and -thiocarbamides and *N*-benzoylformamido-*N'*-arylcarbamides and -thiocarbamides and dimagnetic chelates of these ligands with $MoCl_5$.

Experimental Methods

All the chemicals used were either BDH "Analar" quality or E. Merck "G.R." quality. Alcohol, chloroform, and dimethylformamide were distilled before they were used.

The general method of preparation of ligands *N*,*N*-diphenylformamido-*N''*-phenylthiocarbamide (DPFPTC), *N*,*N*-diphenylformamido-*N''*-phenylcarbamide (DPFPC), *N*,*N*-diphenylformamido-*N''*-*o*-tolylthiocarbamide (DPF-*o*-TTC), *N*,-*N*-diphenylformamido-*N''*-*p*-tolylthiocarbamide (DPF-*p*-TTC), *N*-benzoylformamido-*N'*-phenylthiocarbamide (BFPTC), *N*-benzoylformamido-*N'*-phenylcarbamide (BFPC), *N*-benzoylformamido-*N'*-*o*-tolylthiocarbamide (BF-*o*-TTC), and *N*-benzoylformamido-*N*-*p*-tolylthiocarbamide (BF-*p*-TTC) is summarized as follows. The required symmetrical or asymmetrical guanidines were refluxed for 1.5 h with the appropriate aryl isocyanates or aryl isothiocyanate in 1:1 molar ratio in the alcoholic medium. After the completion of the reaction, excess alcohol was distilled out and the ligand was recovered and recrystallized from hot ethanol.

The symmetrical (a) and asymmetrical (b) guanidines have been synthesized (Sheers, E. H., "Encyclopedia of Chemical Technology" 2nd ed, Vol. 10, Wiley, New York, N.Y., 1966, pp 736, 740.) by the following reactions:



$$H_2N\overset{\overset{NH}{\|}}{C}NH_2 + ArNH_2 \rightarrow ArNH\overset{\overset{NH}{\|}}{C}NHAr$$

guanidine aryl-amines diaryl-guanidines (a)

$$RNH_2 + CNNH_2 \rightarrow RNHC(=NH)NH_2$$

amine cyan-amides b

The interaction of *N*,*N*-Diphenylguanidine (I) with aryl isocyanates and aryl isothiocyanates yields the formation of *N*,-*N'*-diarylformamido-*N''*-arylcarbamides (II) and *N*,*N'*-diarylformamido-*N''*-arylthiocarbamides (III) by the mechanism shown in Scheme I.

On the other hand asymmetrical guanidine IV leads to the formation of products V and VI with aryl isothiocyanates and aryl isocyanate, respectively (Scheme II).

Purity of these ligands was checked by sharp melting point and elemental analysis.

General Method of the Preparation of Complexes

A chloroform solution (0.1 M) of ligand was added drop by drop with constant stirring to a chloroform solution of anhydrous $MoCl_5$ (0.1 M). During the course of reaction temperature was maintained below 10 °C. After completion of the reaction, the reaction mixture was allowed to stand for an hour to attain equilibrium. The colored complexes could be separated by distilling out the excess solvent ($CHCl_3$). Melting points of these

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Table I. IR Spectra of *N,N'*-Diarylformamido-*N''*-arylthiocarbamides and -carbamides and *N*-Benzoylformamido-*N'*-arylthiocarbamides and -carbamides and Their $MoCl_5$ Complexes[a]

Substance	=NH stretch	C=O stretch	N–H bond	C–H stretch	C–N stretch + N–H bond + (C=S) bond	ν(C=S) stretch	C=S stretch
BFPTC	3400 s	1700 m	1680 s	1550 s	1413 s 1470 s	1227 m	716 w
$MlCl_5 \cdot 2BFPTC$	3290 m, g	1700 m	1630 ms	1595 m	1490 w	1215 m	705 m
BFPC	3355 s	1725 m	1685 s	1550 m	1440 s	1280 w	
$MoCl_5 \cdot 2BFPC$		1720 w	1635 vw	1590 m 1550 mb	1490 ms 1440 ms	1255 ms	
BF-*o*-TTC	3400 w	1698 m	1625 s, b	1525 w	1400 m	1175 w 1147 w	750 m
$MoCl_5 \cdot 2$BF-*o*-TTC	3300–3350 w	1698 m	1630 m 1605 m	1575 1520 w	1400 ms	1150 ws	735 m
BF-*p*-TTC	3400 s	1700 m	1625 s	1563 s	1440 m	1282 s	799 w
$MoCl_5 \cdot 2$BF-*p*-TTC	3222–3272 m	1699 m	1620 s	1570 m	1448 wb	1266 s	780 w
DPFPTC	3385 s		1641 vw	1540 s	1441 vw	1225 m	729 m
$MoCl_5 \cdot 2DPFPTC$	3285 mb		1635 s	1585 s	1485 s	1225 m	720 m
DPFPC	3400 s	1735 w	1640 m	1582 m 1540 m	1460 m	1260 m	
$MoCl_5 \cdot 2DPFPC$		1720 w	1635 m	1500 1560 m	1470 w	1255 m	
DPF-*p*-TTC	3400 s		1600 s	1566 m 1542 s	1442 m	1220 m	758 m
$MoCl_5 \cdot 2$DPF-*p*-TTC			1622 1600 w	1575 m	1480 w	1205 b	750 m
DPF-*o*-TTC	3400 s		1660 m	1540 m	1430 s	1270 m	760 b
$MoCl_5 \cdot 2$DPF-*o*-TTC			1650 s	1555 m	1440 s	1260 m	745 m

[a] Key: m = medium, s = strong, b = broad, w = weak.

Table II. Magnetic Susceptibility and Molar Conductance Results of the Complexes

Compound	Magnetic suscep-tibility $10^{-6}\chi$	Molar conductance	
		Molarity, M	Conduc-tance λ_M, mhos
$[MoCl_2(BFPTC)_2]Cl_3$	−0.7045	0.10×10^{-2}	202.50
$[MoCl_2(BF\text{-}p\text{-}TTC)_2]Cl_3$	−0.4903	0.10×10^{-2}	207.60
$[MoCl_2(DPF\text{-}p\text{-}TTC)_2]Cl_3$	−0.5710	0.11×10^{-2}	206.80
$[MoCl_2(DPFPC)_2]Cl_3$	−0.6874	0.11×10^{-2}	215.70
$[MoCl_2(BFPC)_2]Cl_3$	−0.5820	0.12×10^{-2}	197.70
$[MoCl_2(BF\text{-}o\text{-}TTC)_2]Cl_3$	−0.5398	0.11×10^{-2}	198.60
$[MoCl_2(DPF\text{-}o\text{-}TTC)_2]Cl_3$	−0.5541	0.11×10^{-2}	209.30
$[MoCl_2(DPFPTC)_2]Cl_3$	−0.7720	0.12×10^{-2}	192.30

compounds were determined in open capillary tubes on a Unimelt temperature apparatus and are uncorrected. In all the compounds molybdenum, sulfur, and chlorine were estimated quantitatively (*2*, *3*, *5*). The obtained percentage values of these elements are in good agreement with calculated ones for 1:2 complexes.

Complex (M = % calcd (found) [M = Mo, S, Cl]): $MoCl_5 \cdot 2DPFPTC$, Mo = 10.25 (10.38), S = 6.82 (6.95), Cl = 18.93 (19.20); $MoCl_5 \cdot 2DPFPC$, Mo = 10.60 (10.75), Cl = 19.61 (20.20); $MoCl_5 \cdot 2$DPF-*p*-TTC, Mo = 9.95 (10.20), S = 6.63 (6.85), Cl = 18.39 (19.28); $MoCl_5 \cdot 2BFPC$, Mo = 11.80 (11.50), Cl = 21.82 (22.45); $MoCl_5 \cdot 2BFPTC$, Mo = 11.47 (11.12), S = 7.64 (7.50), Cl = 21.19 (21.80); $MoCl_5 \cdot 2$BF-*o*-TTC, Mo = 10.99 (10.75), S = 7.32 (7.42), Cl = 20.32 (20.60); $MoCl_5 \cdot 2$BF-*p*-TTC, Mo = 10.99 (10.70), S = 7.32 (7.43), Cl = 20.32 (20.62); $MoCl_5 \cdot 2$DPF-*o*-TTC; Mo = 9.95 (10.25), S = 6.63 (7.78), Cl = 18.39 (19.05).

The magnetic measurements of these complexes were carried out on a Goy balance at room temperature using a field strength of 4.5×10^3 G. The sample tube was calibrated with mercury tetrathiocyanatocobaltate.

Molar conductance of the complexes was determined in *N,N*-dimethylformamide at a concentration of 10^{-2} M with conductivity meter Type LBR of Wissenschaftlich technisch, Wersstatten, Germany, using a dip type cell.

The infrared spectra of the organic ligands and complexes were recorded in KBr pellets on Perkin-Elmer grating infrared spectrophotometer Models 237-B and 621 in the range of 4000–200 cm^{-1}, using the pellet technique. The spectra are complicated and difficult to interpret; however, only those peaks that could be assigned with reasonable certainty are listed in Tables I and II.

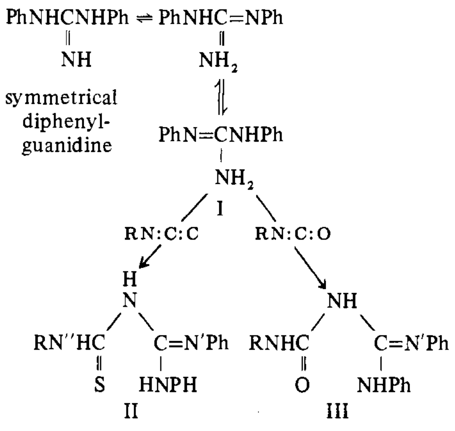
Results and Discussion

All these complexes are colored and sparingly soluble in common organic solvents but are highly soluble in *N,N*-dimethylformamide. All of them are easily decomposed by mineral acids. (The melting range of the complexes is 118–182 °C). Results indicate the $MoCl_5$–ligand ratio as 1:2 which corresponds to the general empirical formula $(MoCl_2L_2)Cl_3$. Very low solubility of these complexes in suitable solvent precluded the molecular weight determination. Magnetic susceptibility of the complexes is found in the range −0.49 to -0.77×10^{-6} g. The negative values of the susceptibility indicate that all the complexes are diamagnetic; all the electrons in these complexes are paired due to metal–metal bonding.

The observed values of molar conductance in DMF are in the range 192.3–209.3 mhos (Table I). The molar conductance results indicate the electrolytic nature of complexes and correspond to 1:3 electrolytes (*8*).

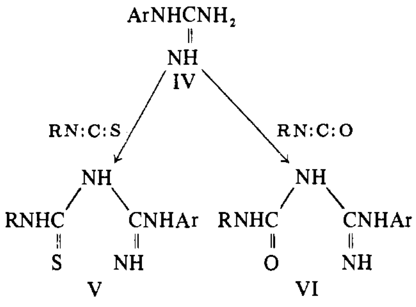
On an examination of infrared spectra of ligands and their metal chelates it can be seen that these ligands exhibit a C=O stretching band of medium intensity in the region 1698–1735 cm^{-1} which is observed to be stronger than the usual ketone C=O band (*6*). On chelation with the metal the carbonyl absorption peak is shifted to lower frequency (5–15 cm^{-1}) of comparatively weak intensity. As there is almost no change in the benzoylic carbonyl frequencies on complexation, the benzoylic C=O group cannot be considered as a site for coordination. A peak at 1400–1490 cm^{-1} is due to a mixed band of (C–N) stretch, N–H bend, and C=S bend. The strong bands at 3355–3400 cm^{-1} in the case of disubstituted formamido-(N''-substituted)thiocarbamides and -carbamides are attributed to N–H stretching of secondary amines (=NH). In complexes either this peak is missing or a broad peak covering a range of 3300–3272 cm^{-1} of comparatively low intensities is obtained.

Scheme I



ph = phenyl; R = phenyl, *o*-toly, *p*-tolyl

Scheme II

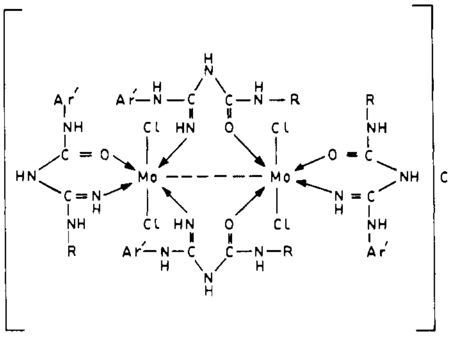


Ar = benzoyl; R = phenyl, *o*-tolyl, *p*-tolyl

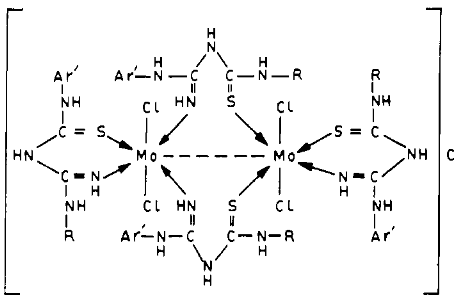
The broad nature of the peaks suggests that bonding between metal and ligands is strong. The infrared spectra of ligands show that BFPTC, BF-*o*-TTC, BF-*p*-TTC, DPFPTC, DPF-*p*-TTC, and DPF-*o*-TTC exhibit a C=S band of medium broad intensity at frequencies 716–799 cm^{-1} which is lowered (8–20 cm^{-1}) on complexation. All these observations show that coordination in the case of BFPTC, BF-*o*-TTC, BF-*p*-TTC, DPFPTC, DPF-*p*-TTC, and DPF-*o*-TTC is through sulfur and nitrogen (of the =NH group) while in the case of BFPC and DPFPC complexes the coordination is through oxygen and nitrogen.

Recent X-ray work (*9*) has shown solid molybdenum(V) chloride to be dimeric with chlorine–chlorine bridges giving the Mo atom in octahedral configuration, but in benzene solution it is monomeric and presumably has the same trigonal-bipyramidal structure as in the vapor phase.

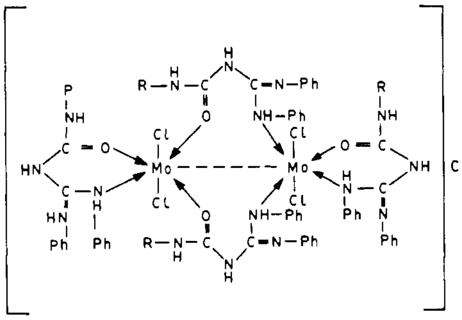
From the experimental results it seems probable that a dimeric complex having octahedral configuration and a metal–metal bond between the two molybdenum atoms is formed. On the basis of magnetic, molar conductance measurements, and elemental analysis the complexes so formed can be represented by the following dimeric structures.



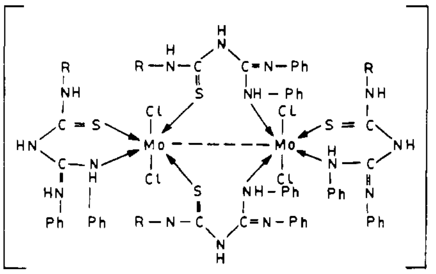
N-benzoylformamido-*N*′-arylcarbamides
$\{[MoCl_2(BFPC)_2]_2\}$: R = $-C_6H_5$, Ar′ = $-C_6H_5CO$



N-benzoylformamido-*N*′-arylthiocarbamides
$\{[MoCl_2(BFPTC)_2]_2\}Cl_6$:
R = $-C_6H_5$, Ar′ = $-C_6H_5CO$
$\{[MoCl_2(BF\text{-}o\text{-}TTC)_2]_2\}Cl_6$:
R = $-C_6H_4-CH_3$ (ortho); Ar′ = $-C_6H_5CO$
$\{[MoCl_2(BF\text{-}p\text{-}TTC)_2]_2\}Cl_6$:
R = $-C_6H_4-CH_3$ (para); Ar′ = $-C_6H_5CO$



N,*N*′-diarylformamido-*N*″-arylcarbamides
$\{[MoCl_2(DPFPC)_2]_2\}Cl_6$: R = $-C_6H_5$, Ph = phenyl



N,*N*-diarylformamido-*N*″-arylthiocarbamides
$\{[MoCl_2(DPFPTC)_2]_2\}Cl_6$:
R = $-C_6H_5$, Ph = phenyl
$\{[MoCl_2(DPF\text{-}o\text{-}TTC)_2]_2\}$:
R = $-C_6H_4-CH_3$ (ortho), Ph = phenyl
$\{[MoCl_2(DPF\text{-}p\text{-}TTC)_2]_2\}Cl_6$:
R = $-C_6H_4-CH_3$ (para), Ph = phenyl

Acknowledgment

Authors are thankful to the authorities of B.I.T.S. Pilani for providing necessary facilities and to the University Grants Commission New Delhi (India) for the award of a fellowship to K.L.M.

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Received for review November 14, 1977. Accepted April 11, 1978.