

## Molybdenum(III) Complexes with Unidentate Nitrogen Donors

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Complexes of stoichiometry  $[\text{MoX}_3\text{L}_3]$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{NCS}^-$  and  $\text{L} = \beta$ -picoline,  $\gamma$ -picoline, piperidine or benzimidazole) have been prepared by the interaction of  $(\text{NH}_4)_2[\text{MoCl}_5\text{H}_2\text{O}]$ ,  $(\text{NH}_4)_2[\text{MoBr}_5\text{H}_2\text{O}]$  and  $(\text{NH}_4)_3[\text{Mo}(\text{NCS})_6]$  with the bases. The complexes are characterized by magnetic and spectral measurements.

THE study of the chemistry of molybdenum(III) is becoming increasingly important because of the suggestions that Mo(III) may be involved in catalysis by nitrogenase<sup>1</sup> and molybdoenzymes<sup>2</sup> and in the reduction of dinitrogen in model experiments<sup>3</sup>. Several complexes of Mo(III) with unidentate nitrogen donors of composition  $[\text{MoCl}_3\text{L}_3]$  ( $\text{L} = \text{py}$ ,  $\text{MeCN}$  or  $\text{PhCN}$ ) have been prepared by exchange reactions of  $\text{K}_3[\text{MoCl}_6]$  with organic ligands<sup>4,5</sup>. Allen and coworkers<sup>6</sup> obtained a series of complexes,  $[\text{MoBr}_3\text{L}_3]$  ( $\text{L} = \text{MeCN}$ ,  $\text{EtCN}$  or  $\text{PrCN}$ ), by treating  $\text{MoBr}_3$  with an excess of appropriate nitrile in a sealed tube at  $150^\circ$ . We have previously reported the preparation, spectral and magnetic properties of Mo(III) with some bidentate nitrogen donors<sup>7</sup>. In the present paper preparation and characterization of the complexes of Mo(III) with some unidentate nitrogen donor heterocyclic bases and benzimidazole are reported.

### Materials and Methods

Ammonium salts of pentachloroaquamolybdate(III), pentabromo-aquamolybdate(III), and hexisothiocyanatomolybdate(III) were prepared by the electrolytic reduction as described in literature<sup>8-10</sup>.

All reactions were carried out in pure and dry nitrogen atmosphere. But the complexes of Mo(III) with picolines were prepared in an ordinary atmosphere as described by Jonassen and Bailin<sup>4</sup> in the preparation of  $[\text{MoCl}_3(\text{py})_3]$ .

*Trichloro-tris( $\gamma$ -picoline)molybdenum(III)*— $(\text{NH}_4)_2[\text{MoCl}_5\text{H}_2\text{O}]$  (2 g) was refluxed with freshly distilled  $\gamma$ -picoline (15 ml) for 4 hr. At the end of the reaction and on cooling, a yellow precipitate in dark brown solution was observed. The products were poured in distilled water (75 ml) and stirred thoroughly for 2 hr. The yellow residue was filtered, washed with water and dried *in vacuo* over KOH (Found: Mo, 20.00; N, 8.88; Cl, 22.30.  $[\text{MoCl}_3(\gamma\text{-pic})_3]$  requires Mo, 19.94; N, 8.87; Cl, 22.11%).

*Trichloro-tris( $\beta$ -picoline)molybdenum(III)*— $(\text{NH}_4)_2[\text{MoCl}_5\text{H}_2\text{O}]$  (0.85 g) was refluxed with freshly

distilled  $\beta$ -picoline (8 ml) for 6 hr. Like the previous experiment the reaction products were stirred thoroughly with distilled water. The yellow solid was filtered, washed with water and dried *in vacuo* over KOH (Found: Mo, 19.86; N, 8.76; Cl, 22.08.  $[\text{MoCl}_3(\beta\text{-pic})_3]$  requires Mo, 19.94; N, 8.87; Cl, 22.11%).

*Tribromo-tris( $\gamma$ -picoline)molybdenum(III)*—This compound was prepared by refluxing ammonium pentabromo-aquamolybdate(III) with  $\gamma$ -picoline and using the conditions identical to those described above (Found: Mo, 15.70; N, 6.78; Br, 39.15.  $[\text{MoBr}_3(\gamma\text{-pic})_3]$  requires Mo, 19.61; N, 6.83; Br, 39.02%).

*Tribromo-tris( $\beta$ -picoline)molybdenum(III)*—This compound was prepared as above from the ammonium pentabromo-aquamolybdate(III) and freshly distilled  $\beta$ -picoline (Found: Mo, 15.67; N, 6.77; Br, 39.16;  $[\text{MoBr}_3(\beta\text{-pic})_3]$  requires Mo, 15.61; N, 6.83; Br, 39.02%).

*Tribromo-tris(piperidine)molybdenum(III)*—Ammonium pentabromo-aquamolybdate(III) (1 g) was kept in a 125 ml flask under dry nitrogen and about 20 ml piperidine distilled into it. It was stirred thoroughly and filtered. The brownish yellow filtrate was kept *in vacuo* over conc.  $\text{H}_2\text{SO}_4$  for 24 hr. The pale yellow solid was filtered, washed with petroleum ether and dried *in vacuo* over KOH/ $\text{CaCl}_2$  (Found: Mo, 16.09; N, 7.14; Br, 40.58.  $[\text{MoBr}_3(\text{pip})_3]$  requires Mo, 16.24; N, 7.11; Br, 40.61%).

*Trisothiocyanato-tris( $\gamma$ -picoline)molybdenum(III)*—A mixture of  $\gamma$ -picoline (10 ml) and  $(\text{NH}_4)_3[\text{Mo}(\text{NCS})_6]$  (0.5 g) was stirred for 3 hr. On dilution with large volume of water, a fine yellow solid was separated from the reaction mixture. The solid was washed with water and dried *in vacuo* over KOH/ $\text{CaCl}_2$  (Found: Mo, 17.52; N, 15.45.  $[\text{Mo}(\text{NCS})_3(\gamma\text{-pic})_3]$  requires Mo, 17.48; N, 15.30%).

*Trisothiocyanato-tris( $\beta$ -picoline)molybdenum(III)*—This compound was prepared as above by the reaction of  $\beta$ -picoline and  $(\text{NH}_4)_3[\text{Mo}(\text{NCS})_6]$  (Found: Mo, 17.56; N, 15.38.  $[\text{Mo}(\text{NCS})_3(\beta\text{-pic})_3]$  requires Mo, 17.48; N, 15.30%).

*Trisothiocyanato-tris(piperidine)molybdenum(III)* —  $(\text{NH}_4)_3[\text{Mo}(\text{NCS})_6]$  (0.8 g) was allowed to react with piperidine (15 ml) in dry nitrogen atmosphere for 8 hr with constant stirring. The yellowish red solution was filtered and the filtrate kept *in vacuo* over conc.  $\text{H}_2\text{SO}_4$  for 24 hr. The separated yellow solid was filtered, washed with minimum volume of water-ethanol (2:1) and dried *in vacuo* over  $\text{KOH}/\text{CaCl}_2$  (Found: Mo, 18.18; N, 16.10.  $[\text{Mo}(\text{NCS})_3(\text{pip})_3]$  requires Mo, 18.28; N, 16.00%).

*Trisothiocyanato-tris(benzimidazole)molybdenum(III)* — A solution of 0.5 g (1 mole) ammonium hexisothiocyanatomolybdate(III) in 15 ml methanol was stirred thoroughly with 0.36 g (3 moles) benzimidazole dissolved in 10 ml methanol under nitrogen atmosphere. When deepening of yellow colour took place, it was filtered and the filtrate diluted with large volume of water until a deep yellow solid separated. It was filtered, washed with water-ethanol (1:1) and dried *in vacuo* over  $\text{KOH}/\text{CaCl}_2$  (Found: Mo, 15.42; N, 20.22.  $[\text{Mo}(\text{NCS})_3(\text{BzH})_3]$  requires Mo, 15.38; N, 20.19%).

*Physical measurements* — Conductivity measurements were made with WTW conductivity meter, type LBR. Magnetic susceptibilities were measured on a Gouy magnetic balance at room temperature; diamagnetic corrections were made using Pascal's constants<sup>11</sup>. The electronic absorption spectra of the solutions were measured on a Hilger and Watts Uvispek spectrophotometer model No. H 700 with silica prism. A Hilger-Uvispek standard reflectance attachment was used to measure the reflectance spectra, with  $\text{MgCO}_3$  as reference. IR spectra were recorded on Perkin-Elmer 237 and 621 recording spectrophotometers with samples mounted in KBr discs.

## Results and Discussion

Reaction of  $\beta$ - or  $\gamma$ -picoline with ammonium salts of pentachloroaquamolybdate(III) or pentabromo-aquamolybdate(III) at reflux temperature leads to the isolation of heterocomplexes of composition  $[\text{MoX}_3\text{L}_3]$  ( $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$  and  $\text{L} = \beta$ - or  $\gamma$ -picoline). Ammonium hexisothiocyanatomolybdate(III) also reacts with  $\beta$ - and  $\gamma$ -picolines, on stirring in the cold with appropriate amount of ligands to form complexes  $[\text{Mo}(\text{NCS})_3(\beta\text{-pic})_3]$  and  $[\text{Mo}(\text{NCS})_3(\gamma\text{-pic})_3]$  respectively.

$\alpha$ -Picoline does not react similarly, probably because of steric hindrance caused by 2-methyl substituent. Piperidine reacts with  $(\text{NH}_4)_2[\text{MoBr}_5\text{H}_2\text{O}]$  under nitrogen atmosphere and  $(\text{NH}_4)_3[\text{Mo}(\text{NCS})_6]$  in cold forming  $[\text{MoX}_3(\text{pip})_3]$  ( $\text{X} = \text{Br}^-$  or  $\text{NCS}^-$ ). But  $(\text{NH}_4)_2[\text{MoCl}_5\text{H}_2\text{O}]$  fails to form complex of definite composition with piperidine owing to rapid hydrolysis of ammonium pentachloro-aquamolybdate(III). At the reflux temperature pentabromo-aquamolybdate(III) and hexisothiocyanatomolybdate(III) are also hydrolysed which may be due to greater basicity of piperidine ( $pK_a = 11.13$ ).

Benzimidazole ( $\text{BzH} = \text{C}_7\text{H}_6\text{N}_2$ ) replaces three of the six thiocyanate groups in ammonium hexisothiocyanatomolybdate(III) in methanol under purified nitrogen atmosphere, forming a complex  $[\text{Mo}(\text{NCS})_3(\text{BzH})_3]$ . The tris-benzimidazole ligated

complex is insoluble in water and is precipitated as a deep yellow crystalline solid from the methanolic reaction mixture on dilution with water.

All these complexes are fairly stable in air and are sparingly soluble in water. An aqueous suspension of the piperidine complexes of Mo(III) is gradually hydrolysed giving a brownish black precipitate of indefinite composition. The complexes are slightly soluble in ethanol and acetone but fairly soluble in methanol. The methanolic solutions of the complexes  $[\text{MoX}_3\text{L}_3]$  are almost non-conducting indicating the non-electrolytic nature of these complexes.

The effective magnetic moment values of the complexes at room temperature (300°K) are in the range 3.7-3.85 BM (Table 1) as expected for the spin only value for a  $t_{2g}^3$  configuration<sup>12</sup>, suggesting an octahedral arrangement of the ligand molecules around Mo(III) ions.

The tris-ligated complexes of picolines, piperidine and benzimidazole exhibit an intense charge transfer band near 24000-27000  $\text{cm}^{-1}$  (Table 1). The  $d-d$  transitions of the complexes of the type  $[\text{MoX}_3\text{L}_3]$  are probably obscured by extended tail of the charge transfer band.

The IR spectra of  $[\text{MoX}_3(\gamma\text{-pic})_3]$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{NCS}^-$ ) exhibit a band at  $\sim 1020\text{-}1025 \text{ cm}^{-1}$  which is absent in the free  $\gamma$ -picoline and is attributed to the shift of symmetric ring breathing mode (997  $\text{cm}^{-1}$ ) of the free ligand. Graddon and coworkers<sup>13</sup> observed the same pattern of shifts in octahedral complexes of cobalt(II) with  $\gamma$ -picoline. The shift of a strong band at 1608  $\text{cm}^{-1}$  in  $\gamma$ -picoline and 1580  $\text{cm}^{-1}$  in  $\beta$ -picoline to the higher frequency, 1615-1628  $\text{cm}^{-1}$  and 1602-1615  $\text{cm}^{-1}$  respectively are diagnostic of coordination of  $\gamma$ - and  $\beta$ -picolines.

In the case of  $[\text{MoX}_3(\text{pip})_3]$  ( $\text{X} = \text{Br}^-$  or  $\text{NCS}^-$ ) the absorption bands at 1445-1450  $\text{cm}^{-1}$  and 866-870  $\text{cm}^{-1}$  can be assigned -N-H asymmetric and N-H deformation frequencies respectively. When compared with -N-H asymmetric (1440  $\text{cm}^{-1}$ ) and N-H deformation (860  $\text{cm}^{-1}$ ) bands of the free piperidine we find a shift to higher frequencies in both the bands which is in agreement with the observation of Svatos and coworkers<sup>14</sup>.

TABLE 1 — MAGNETIC MOMENTS AND REFLECTANCE SPECTRAL DATA OF THE COMPLEXES

Complex	Colour	$\mu_{\text{eff}}$ B.M.	$\lambda_{\text{max}}(\text{cm}^{-1})^*$ (C-T)
$\text{MoCl}_3(\gamma\text{-pic})_3$	Yellow	3.77	25641 (25773) ( $\epsilon_{\text{max}} = 3050$ )
$[\text{MoCl}_3(\beta\text{-pic})_3]$	do	3.77	26316
$[\text{MoBr}_3(\gamma\text{-pic})_3]$	do	3.78	25974
$[\text{MoBr}_3(\beta\text{-pic})_3]$	do	3.76	26316 (26667) ( $\epsilon_{\text{max}} = 3120$ )
$[\text{MoBr}_3(\text{pip})_3]$	Pale yellow	3.73	27027
$[\text{Mo}(\text{NCS})_3(\gamma\text{-pic})_3]$	Yellow	3.78	27027
$[\text{Mo}(\text{NCS})_3(\beta\text{-pic})_3]$	do	3.75	27027
$[\text{Mo}(\text{NCS})_3(\text{pip})_3]$	do	3.77	27027 (27322) ( $\epsilon_{\text{max}} = 3200$ )
$[\text{Mo}(\text{NCS})_3(\text{BzH})_3]$	Deep yellow	3.77	24390 (24570) ( $\epsilon_{\text{max}} = 2860$ )

\*The band positions within parentheses are in chloroform.

The  $\nu$ C-N and  $\nu$ C-S of the complexes occur in the appropriate range around 2070 and 815  $\text{cm}^{-1}$  respectively for N-bonded thiocyanate<sup>15</sup>. In the case of  $[\text{Mo}(\text{NCS})_3(\gamma\text{-pic})_3]$  and  $[\text{Mo}(\text{NCS})_3(\text{pip})_3]$ , the  $\delta$ N-C-S occurs at 472 and 474  $\text{cm}^{-1}$  respectively which further supports Mo-NCS bonding<sup>16</sup>. The  $\nu$ Mo-N vibrations in these complexes are recorded at 280 and 282  $\text{cm}^{-1}$  respectively.

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