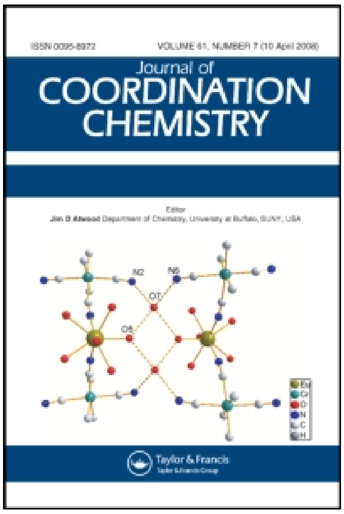

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PENTACOORDINATE CATIONIC MOLYBDENUM(I) COMPLEXES

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COMMUNICATION

PENTACOORDINATE CATIONIC MOLYBDENUM(I) COMPLEXES

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The nitrosylmolybdenum complexes so far characterized, and which contain formally Mo(I), have a coordination number of six.[1,2] The hexacoordinate structure of $Cs_2[Mo(NO)Cl_4(H_2O)]$, as predicted by vibrational spectroscopy[1], was confirmed by X-ray structural determination.[3] The $\{MoNO\}^4$ group has been stabilized by several geometries ranging from a five to a seven coordination number.[3-5] Interestingly, these complexes show 14-, 16- and 18-electron configurations. The $\{MoNO\}^5$ group so far has been stabilized by hexacoordination having a 17-electron configuration. The present report deals with the synthesis and characterization of $[Mo(NO)(L\text{-}L)_2]Cl_2$ (L-L = phen or bipy) with pentacoordination and having a 15-electron configuration. Five coordination is hitherto unknown for Mo(I) complexes.

The title complexes were synthesized by refluxing $K_4[Mo(NO)(CN)_5]\cdot 2H_2O$ (2.0 g) in 50 cm^3 concentrated hydrochloric acid in an oxygen-free atmosphere and adding phenantrholine (2.8 g) dissolved in a little concentrated hydrochloric acid to the greenish red solution. Any immediate precipitate was quickly filtered off and the greenish-red filtrate was refluxed for another 15 min whereby a deep bluish-green precipitate settled at the bottom. The mixture was cooled at room temperature and stood for 2 hrs. The solid filtered under suction, washed with hydrochloric acid and dried over KOH *in vacuo*. *Yield*: 2.2 g. *Anal.*; Calcd. for $MoC_{24}H_{16}N_5Cl_2O$: C, 51.71; H, 2.87; N, 12.56; Cl, 12.73%. Found: C, 51.80; H, 2.06; N, 12.43; Cl, 12.33%.

The corresponding bipyridyl analogue, $[Mo(NO)(bipy)_2]Cl_2$ was synthesized similarly using 2,2'-bipyridine (2.3 g), instead of phenanthroline. The bipyridyl derivative crystallized as dark bluish green crystals on standing overnight. This derivative is more soluble than the phenanthroline analogue and the yield is correspondingly low (0.7 g). *Anal*; Calcd. for $MoC_{20}H_{16}N_5Cl_2O$: C, 47.16; H, 3.14; N, 13.76; Cl, 13.93%. Found: C, 47.34; H, 2.95; N, 13.45; Cl, 13.68%.

These complexes are susceptible to air oxidation, especially in solution. In deoxygenated water or dilute hydrochloric acid, they dissolve slowly to give a purple solution. Spectroscopic data for these derivatives along with $Cs_2[Mo(NO)Cl_4(H_2O)]$ are presented in Table I. The Mo hyperfine value of the hexacoordinated complex in an earlier ESR study[1] was obviously in error and was redetermined. The i.r. spectra of the two species do not show any vibration in the range 350 to 250 cm^{-1} assignable to ν(Mo–Cl) where a strong stretching vibration is expected if there is a Mo–Cl bond.[1,6,7] This observation is consistent with the molar conductance values obtained for these complexes in aqueous medium ($\Lambda_M = 240$ mho cm^2 mol^{-1} for the phen, and $\Lambda_M = 245$ mho cm^2 mol^{-1} for the bipy derivatives, respectively).

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TABLE I
Characteristic data for the complexes.

Compound	ν(NO)[a] (cm^{-1})	$g_{\perp}$[b]	$g_{\parallel}$[b]	$\langle g \rangle$[c]	$\langle A \rangle$[c]	Ref.
$Cs_2[Mo(NO)Cl_4(H_2O)]$	1622(vs)	1.99	1.91	1.96	55 G	This work
	1622(vs)	1.99	1.90	1.95	23 G	1
$[Mo(NO)(phen)_2]Cl_2$	1545(vs)	1.97	1.92	1.97	50 G	This work
$[Mo(NO)(bipy)_2]Cl_2$	1555(vs)	1.97	1.92	1.97	50 G	This work

[a]In KBr: [b]In solid: [c]In 6 M HCl.

Thus these complexes are pentacoordinate in nature. The effective magnetic moments of $[Mo(NO)(phen)_2]Cl_2$ and $[Mo(NO)(bipy)_2]Cl_2$ are 1.68 BM and 1.70 BM, respectively. The deviation of the expected magnetic moment value (of the order of 2.3 BM at 300° K) shows considerable distortion from a regular structure.[8] The ESR line shape, even at room temperature, of these complexes suggests a tetragonally-distorted structure. As the g-tensor values observed are in the order $g_{\perp} > g_{\parallel}$, the unpaired electron must be in the nonbonding d_{xy} orbital.[9] As expected no ^{14}N (NO) hyperfine splittings are observed. The absence of ^{14}N hyperfine splittings by the interaction of the coordinated aromatic diimines suggest the approach of these *N*-donors through the nodal plane of d_{xy} orbital of Mo. Thus, the geometry of these complexes is square pyramidal.

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