Heptakis(alkyl isocyanide)molybdenum(II) Complexes

By Miroslav Novotny and Stephen J. Lippard*
(*Department of Chemistry, Columbia University, New York* 10027)

Summary The synthesis of $[Mo(CNR)_7]X_2$ (R = Me, X = I^-; R = Bu^t, X = PF_6^-, I_3^-) compounds from $Mo(CO)_6$ or $Ag_4[Mo(CN)_8]$ is described; conductivity and spectral data suggest the presence of seven-co-ordinate molybdenum(II) dications in solution.

Many seven-co-ordinate complexes have been synthesized and studied,[1] but few molecules containing seven identical monodentate ligands bound to a central transition-metal atom have been well characterized.[2] Recent works in our laboratory[3] and elsewhere[4] has led to the preparation of $[Mo(CNR)_6I]I$ and $Mo(CNR)_5X_2$ (X = Br^-, Cl^-) compounds. We report here the synthesis and properties of the parent heptaco-ordinate dications, $[Mo(CNR)_7]^{2+}$.

Compound[a]	ν_{CN}/cm^{-1} [b]	λ_{max}/nm[c]
$Mo(CNR)_7X_2$		
R = Me, X = I^-	2157	402(3·03), 275(4·26) 243(4·52), 221(4·62)
R = Bu^t, X = PF_6^-	2138	413(3·02), 275(4·42) 248(4·53)
R = Bu^t, X = I_3^-	2143	
$Mo(CNR)_6I_2\cdot H_2O$	2119	406(2·61), 275(4·34)
R = Bu^t		*ca.* 240(sh), 218(4·62)
$Mo(CNR)_5Br_2$[d]	2097	
R = *p*-MeC_6H_4		

[a] All new compounds were characterized by analysis for at least four elements. [b] I.r. spectrum in Nujol mull or KBr pellet; bands were typically very broad and strong with both high and low frequency shoulders. [c] U.v.–visible spectra of solutions in methanol. Numbers in parentheses are log ϵ_{max}. [d] Average value from ref. 4.

A mixture containing 2 mmol of $Mo(CO)_6$, 2 mmol of I_2' an excess (21 mmol) of alkyl isocyanide, and 40 ml of methanol was heated to reflux for 5 h under nitrogen. The resultant bright yellow-brown solution was cooled to room temperature, and 150 ml of Et_2O added. After several hours at 0°, yellow crystals of $[Mo(CNMe)_7]I_2$ formed and were recrystallized from methanol–ether. The t-butyl isocyanide analogue was obtained as the hexafluorophosphate salt when a methanolic solution of $NaPF_6$ was added to the yellow-brown solution. Yields were 30—40%.

An alternative route to the t-butyl derivative was discovered during attempts to reproduce the synthesis[3] of $[Mo(CNR)_6I]I$. A mixture of 10 mmol of $Ag_4Mo(CN)_8$ and 30 mmol of AgCN was alkylated with excess (543 mmol) of Bu^tI in 50 ml of chloroform. Dark brown-violet crystals of unknown composition were formed after stirring for several days in the dark at room temperature and allowing the filtrate to evaporate slowly in the air for two weeks. Although this synthesis is completely reproducible, the true chemical nature of the iodine-rich product is not yet known. Recrystallization four times from hot methanol, however, produced dark red crystals of $[(Bu^tNC)_7Mo](I_3)_2$. Furthermore, when the iodine-rich product was dissolved in methylene chloride, washed with aqueous thiosulphate, and the solution treated with Et_2O at 0°, reasonable quantities of $[(Bu^tNC)_6MoI]I\cdot H_2O$ could be isolated.

Spectral properties of the new $[Mo(CNR)_7]^{2+}$ and related complexes are summarized in the Table. The trend in the average C≡N stretching frequency for the series $Mo(CNR)_7^{2+} > Mo(CNR)_6I^+ > Mo(CNR)_5X_2$ is consistent with the expected increase in π-back bonding with decreasing positive charge and number of π-acceptor ligands. Conductivity data indicate the $Mo(CNR)_7X_2$ compounds to be 2 : 1 electrolytes in nitromethane solution. This result and the similarity of the electronic spectral bands for $[Mo(CNR)_7]^{2+}$ and $[Mo(CNR)_6I]^+$ indicate seven-co-ordination. *X*-Ray structural studies of the crystalline solids are in progress.

We thank the National Science Foundation for financial support.

(*Received*, 28*th December* 1972; *Com.* 2137.)

---

[1] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109; M. G. B. Drew and A. P. Walters, *J.C.S. Chem. Comm.*, 1972, 475; A. Mawby and G. E. Pringle, *J. Inorg. Nuclear Chem.*, 1972, **34**, 517, and references therein.
[2] R. L. R. Towns and R. A. Levenson, *J. Amer. Chem. Soc.*, 1972, **94**, 4346.
[3] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.
[4] F. Bonati and G. Minghetti, *Inorg. Chem.*, 1970, **9**, 2642.