Table VI. Possible Infrared Peak Assignments

Unit	ν_3, cm^{-1}	Mean ν_3
$\square O\rightarrow U\leftarrow O\square$	930, 890	910
$Na^+O\rightarrow U\leftarrow O\square$	912 (+895?)	904
$Na^+O\rightarrow U\leftarrow ONa^+$	900 (905 + 895)	900

$O\rightarrow U\leftarrow O$ unit becomes coordinated to one sodium ion, it seems likely that the $\square O\rightarrow U\leftarrow ONa^+$ grouping gives rise to the ν_3 doublet indicated, one component of which is at approximately 895 cm^{-1}. The assignment implies that both the splitting of the uranyl band and the mean frequency decrease as the sodium content increases. It accounts for the fact that the absorption at 890 cm^{-1} does not decrease in intensity (unlike the 930-cm^{-1} band), as the vacancies are filled, but merely appears to shift to slightly higher frequency as the peak at 895 cm^{-1} becomes more intense.

Oxidized and Reduced Bronzes. The behavior of the bronze on oxidation and reduction gives rise to related phases which can be easily understood. We wish to make, however, two additional comments. For the oxidized samples, the composition range observed extends beyond the composition $Na_2O\cdot 13UO_3$ reported by Carnall, *et al.*[3] We did not, however, find the extra X-ray reflections they describe, although the infrared spectrum of their phase is very similar to ours at the same composition. In the reduced bronzes, it is interesting to note that when the vacancy (or sodium ion) concentration exceeds about 5%, the system appears to adopt the $M_{22}O_{58}$ unit cell (*cf.* α-UO_3, the bronze and the oxidized bronze) in preference to the M_6O_{16} cell of α-U_3O_8. The stability of the $M_{22}O_{58}$ cell is substantiated by the fact that once all the vacant uranium sites are filled with sodium, additional sodium is not incorporated by substitution for uranium, giving a reduced O/M ratio (*cf.* L-Ta_2O_5). Instead, a new phase forms which appears to be related to $Na_2U_2O_7$. In the latter compound, sodium ions are situated *interstitially* between the pseudo-hexagonal layers of uranium atoms.

Acknowledgment. We thank the Science Research Council and A.E.R.E. Harwell for the provision of neutron diffraction facilities and the University Support Group for some experimental assistance.

Registry No. UO_3, 1344-58-7; Na_xUO_3, 39390-02-8.

Notes

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Reactions of Octacyanomolybdate(IV). III. Infrared and Magnetic Studies of Compounds with Divalent First-Row Transition Metals

George F. McKnight and Gilbert P. Haight, Jr.*

Received April 16, 1973

Previously there have been systematic studies of six-coordinate transition metal complexes of cyanide[1-4] but little work in the area of eight-coordinate cyanide complexes appears to have been done. Except for $K_4Mo(CN)_8\cdot 2H_2O$ little attention has been given to the spectral, magnetic, and structural properties of the salts of the octacyanomolybdate(IV) ion, specificially those of the divalent first-row transition metals.[5,6] In this note we report the results of infrared and magnetic studies of the series of compounds $M_2Mo(CN)_8\cdot nH_2O$, where $M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$, and Zn^{2+} and n varies from 2 to 9 depending on the cation in question. The results are disappointing in their lack of definition but emphasize the weakness of interactions with $Mo(CN)_8{}^{4-}$.

Experimental Section

Reagents and Physical Measurements. Potassium octacyanomolybdate(IV) was prepared by the method of Furman and Miller[7] from reagent grade materials. The divalent cation salts were of reagent grade and were used without further purification. Chemical microanalyses were performed by the Microanalytical Laboratory of the University of Illinois. Infrared spectra of the solid samples as Nujol mulls were recorded in the cyanide stretching region on a Beckman IR-7 spectrophotometer. Magnetic moments were determined by the Gouy method utilizing an electromagnet and a Sartorius 2403 balance with $Hg[Co(CNS)_4]$ as a standard.[8]

Hydrated Divalent Salts of Octacyanomolybdate(IV). All the divalent salts were prepared essentially in the same manner. Approximately 0.02 mol of the chloride salt (except for Cu^{2+}, where $CuSO_4$ was used) was dissolved in *ca.* 50 ml of distilled water. To each of the solutions was added 25 ml of freshly prepared 0.25 *M* $K_4Mo(CN)_8\cdot 2H_2O$. In all cases except Mn^{2+} an immediate precipitate formed [$Mn_2Mo(CN)_8\cdot 8H_2O$ required *ca.* 10 min standing time before precipitation occurred]. The solids were collected by filtration, washed with acetone, and vacuum dried.

Zinc Octacyanomolybdate(IV)-2-Water. *Anal.* Calcd for $Zn_2Mo(CN)_8\cdot 2H_2O$: C, 20.40; H, 0.85; Zn, 27.76. Found: C, 20.88; H, 0.76; Zn, 27.76.

Copper Octacyanomolybdate(IV)-6.5-Water.[9] *Anal.* Calcd for $Cu_2Mo(CN)_8\cdot 6.5H_2O$: C, 17.52; H, 2.39; Cu, 23.17. Found: C, 17.11; H, 2.39; Cu, 23.25.

Nickel Octacyanomolybdate(IV)-9-Water.[9] *Anal.* Calcd for $Ni_2Mo(CN)_8\cdot 9H_2O$: C, 16.46; H, 3.10; Ni, 20.11. Found: C, 16.57; H, 2.90; Ni, 19.95.

Cobalt Octacyanomolybdate(IV)-9-Water.[9] *Anal.* Calcd for $Co_2Mo(CN)_8\cdot 9H_2O$: C, 16.45; H, 3.11; Co, 20.17. Found: C, 16.81; H, 3.12; Co, 19.75.

Iron(II) Octacyanomolybdate(IV)-7.5-Water.[9] *Anal.* Calcd for $Fe_2Mo(CN)_8\cdot 7.5H_2O$: C, 17.44; H, 2.74; Fe, 20.27. Found: C, 17.70; H, 2.64; Fe, 19.99.

Manganese Octacyanomolybdate(IV)-8-Water. *Anal.* Calcd for $Mn_2Mo(CN)_8\cdot 8H_2O$: C, 17.22; H, 2.89; Mn, 19.69. Found: C, 16.99; H, 2.83; Mn, 19.99.

Results and Discussion

Infrared Spectra. Figure 1 shows the infrared spectra of $K_4Mo(CN)_8\cdot 2H_2O$ and $Ni_2Mo(CN)_8\cdot 9H_2O$ in the cyanide stretching region. The infrared absorbances of these com-

---

(1) D. F. Shriver, A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 4, 725 (1965).

(2) M. G. Emschwiller, *C. R. Acad. Sci.*, 238, 1414 (1954).

(3) J. Richardson and N. Elliot, *J. Amer. Chem. Soc.*, 62, 3182 (1940).

(4) P. G. Salvadeo, *Gazz. Chim. Ital.*, 89, 2184 (1959).

(5) W. U. Malik, *Bull. Chem. Soc. Jap.*, 34, 1306 (1961).

(6) W. U. Malik, *Bull. Chem. Soc. Jap.*, 34, 1310 (1961).

(7) N. H. Furman and C. O. Miller, *Inorg. Syn.*, 3, 160 (1950).

(8) J. Lewis and B. N. Figgis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, 1960, Chapter 6.

(9) More recent preparations indicate that the water content is variable. The number of moles of water per mole of Mo in the Fe^{2+}, Co^{2+}, and Ni^{2+} compounds most recently prepared is 8 while a recent Cu^{2+} preparation contains 5 mol of water per mole of Mo.

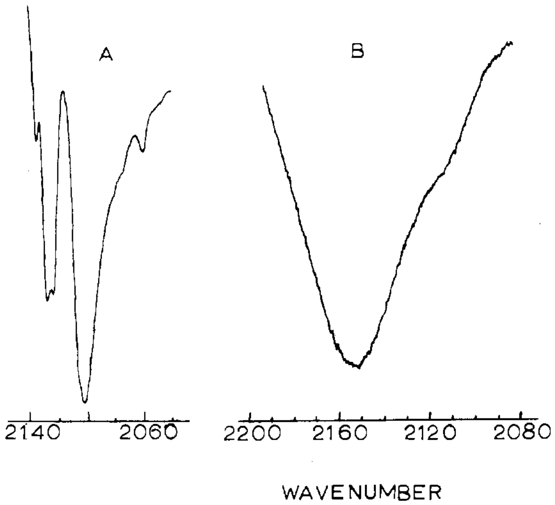

Figure 1. Infrared spectra of the cyanide stretching region of (A) $K_4[Mo(CN)_8]\cdot 2H_2O$ and (B) $Ni_2[Mo(CN)_8]\cdot 9H_2O$.

Table I. Cyanide Stretching Frequencies (cm^{-1}) of Some Divalent Transition Metal Compounds of the Octacyanomolybdate(IV) Ion

$K_4Mo(CN)_8\cdot 2H_2O$	2130 m	2126 s	2120 s	*2103* vs[b]	2060 w
$Mn_2Mo(CN)_8\cdot 8H_2O$		2161 sh	2145 sh	*2128* vs[a]	
$Fe_2Mo(CN)_8\cdot 7.5H_2O$		*2137* m			
$Co_2Mo(CN)_8\cdot 9H_2O$	*2141* m	2118 sh			
$Ni_2Mo(CN)_8\cdot 9H_2O$	*2157* s	2110 sh			
$Cu_2Mo(CN)_8\cdot 6.5H_2O$	*2166* s				
$Zn_2Mo(CN)_8\cdot 2H_2O$	*2170* vs	2195 sh			

[a] Spectra of hydrated and anhydrous salts were identical except for $Mn_2Mo(CN)_8$ where anhydrous salt gave three bands at 2090 (s), 2131 (w), and 2174 (m). [b] Maximum absorbance in italics.

pounds as well as the remaining divalent salts of the octacyanomolybdate(IV) ion are listed in Table I. The spectrum of $K_4Mo(CN)_8\cdot 2H_2O$ exhibits two main peaks at 2103 and 2126 cm^{-1}, respectively, with satellite peaks at 2060 and 2136 cm^{-1}. The spectra of the divalent salts show significant broadening of the cyanide stretching bands. The centers of the broad envelopes are shifted to higher frequencies relative to the principal band of $K_4Mo(CN)_8\cdot 2H_2O$. The greatest shift is found for the Zn^{2+} salt and the shift appears to decrease monotonically across the transition series from Zn^{2+} to Mn^{2+}. Allen and Lippard[10] found that the C≡N stretching band appeared as a broad envelope centered at 2140 cm^{-1} for the compound $(UO_2)_2Mo(CN)_8\cdot nH_2O$ where $n = 6$-8. They attributed this broadening to the formation of cyanide bridges such as $Mo\text{-}C{\equiv}N\text{-}UO_2$. Shriver[11] found that addition of BF_3 to the cyanometalates caused a broadening of the C≡N stretching band and a shift of the band to higher frequency. Wilkinson,[12] *et al.*, found broadening of the C≡N stretching band in some anhydrous complex cyanide acids. They attributed this broadening to protonation of the nitrogen end of the cyanide ligand. Wilmarth, *et al.*,[13] report that a bridging cyanide will absorb at a higher frequency than a corresponding terminal cyanide. Here Emschwiller[2] found that while potassium ferrocyanide, which contains no cyanide bridges, absorbed at 2047 cm^{-1} the heavy metal ferrocyanides gave C≡N stretching bands at 2080 ± 15 cm^{-1}.

Table II. Magnetic Moments (BM) of the Divalent Compounds of the Octacyanomolybdate(IV) Ion

Compound	Av μ/M^{2+}	Spin-only μ
$Zn_2Mo(CN)_8\cdot 2H_2O$	Diamagnetic	
$Cu_2Mo(CN)_8\cdot 6.5H_2O$	1.89 ± 0.04	1.73
$Ni_2Mo(CN)_8\cdot 9H_2O$	3.21 ± 0.04	2.83
$Co_2Mo(CN)_8\cdot 9H_2O$	4.92 ± 0.05	3.88
$Fe_2Mo(CN)_8\cdot 7.5H_2O$	5.05 ± 0.05	4.90
$Mn_2Mo(CN)_8\cdot 8H_2O$	5.94 ± 0.06	5.92

If bridging of the cyanide ligand in octahedral transition metal cyanide complexes results in a broadening of the C≡N stretching band and a shift of the band to higher frequency, then it appears that first row divalent transition metal ions coordinate to N forming -NC- bridged bonds to Mo(IV) in $Mo(CN)_8{}^{4-}$.

Magnetic Moments. In Table II are listed the magnetic moments per metal cation, μ/M^{2+}, calculated for each of the complexes at 25° and at field strengths between 1000 and 6000 G. No variation of μ with field strength was detectable. All of the compounds except the Zn^{2+} compound exhibit some degree of paramagnetism. Magnetic behavior of all compounds is consistent with $Mo(CN)_8{}^{4-}$ remaining diamagnetic. For each of the cations, the moment obtained for the octacyanomolybdate(IV) compound falls within the experimental range of moments which have been found for that cation when it is surrounded by a weak octahedral or tetrahedral ligand field. Figgis and Lewis[14] have estimated the moments which the various first-row divalent transition metal ions in the high-spin state should exhibit in octahedral and tetrahedral fields, but their calculations have been confirmed only for Ni^{2+} and Co^{2+} compounds.

The experimental moments for the Cu^{2+}, Ni^{2+}, and Co^{2+} compounds are closer to the moments expected for these ions in an octahedral field. Although the moment of the Fe^{2+} compound is closer to that expected theoretically for a tetrahedral field, no adequate precedent exists for the use of magnetic moments to distinguish among structures in Cu^{2+} and Fe^{2+} complexes. Fe^{2+} moments vary from 5.1 to 5.7. The experimental value observed here is actually very close to the spin-only value of 4.90 BM.

The results of the present study indicate that the divalent first row transition metal compounds of the octacyanomolybdate(IV) ion prepared exist as polymers where the cyanide ligand acts as a weak bridge between the cation and the Mo^{4+} ion.

There is no compelling evidence that the structure of $Mo(CN)_8{}^{4-}$ is materially affected by this association nor that the divalent ions are not present in their usual state of octahedral coordination. The results are consistent with previous findings that $Mo(CN)_8{}^{4-}$ is an extremely weak Lewis base.[15]

Acknowledgment. This work was supported in part by the National Institutes of Health and the National Science Foundation.

Registry No. $K_4Mo(CN)_8$, 17456-18-7; $Mn_2Mo(CN)_8$, 26042-72-8; $Fe_2Mo(CN)_8$, 34446-92-9; $Co_2Mo(CN)_8$, 34446-93-0; $Ni_2Mo(CN)_8$, 34446-94-1; $Cu_2Mo(CN)_8$, 34446-95-2; $Zn_2Mo(CN)_8$, 34446-96-3.

(10) M. Allen and S. Lippard, *Inorg. Chem.*, 9, 991 (1970).
(11) D. F. Shriver, *J. Amer. Chem. Soc.*, 85, 1405 (1963).
(12) D. F. Evans, D. Jones, and G. Wilkinson, *J. Chem. Soc.*, 3164 (1964).
(13) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, 21, 33 (1961).
(14) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 37 (1964).
(15) G. F. McKnight and G. P. Haight, Jr., *Inorg. Chem.*, 12, 1619, 1934 (1973).