which are in part ligand-to-metal or which involve orbitals containing both metal and ligand character. The high-energy shoulder at about 6 eV is assigned to a ligand–ligand and/or ligand–metal transition.

From the partial MO diagram of $Fe(CO)_5$, low-energy metal-to-ligand transitions are expected, since unoccupied MO's with a_2' symmetry, which are purely ligand nonbonding orbitals, are energetically low lying.

Further commentary and comparison between calculated and observed electronic spectra must await more extensive experimental work. Experimental data on the electronic spectra of transition metal carbonyls are quite incomplete. There is as yet no work dealing with the low-temperature spectra, on the basis of which it might be possible to decide questions relating to vibronically allowed transitions.

The Structure of the *trans*-Dioxotetracyanomolybdate(IV) Ion in the Crystalline Salt $NaK_3MoO_2(CN)_4 \cdot 6H_2O$[1,2]

V. W. Day[3] and J. L. Hoard[4]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received December 7, 1967*

Abstract: A three-dimensional X-ray analysis of structure for crystals conforming in preparative method, composition, and color to the classic specifications for a salt presumed to contain the eight-coordinate $Mo(OH)_4(CN)_4^{4-}$ ion demonstrates that the complexed species is in fact the octahedral *trans*-dioxotetracyanomolybdate(IV) ion, $MoO_2(CN)_4^{4-}$. These structural data and the recent study by Lippard and Russ together suggest that the $Mo(OH)_4(CN)_4^{4-}$ ion is not a stable species either in crystals or in solution. The orthorhombic unit cell of crystalline $NK_3MoO_2(CN)_4 \cdot 6H_2O$ has $a = 12.46$, $b = 7.16$, $c = 9.17$ Å, and contains two formula weights; the space group is Pmna-D_{2h}^7. Visually estimated cross-correlated intensities for 931 independent nonvanishing reflections recorded photographically with Mo Kα radiation, approximately the number of data comprised in the Cu Kα limiting sphere, were employed to determine structure; anisotropic full-matrix least-squares refinement led to $R = 0.078$. The red $MoO_2(CN)_4^{4-}$ ion, completely vulnerable to hydrolysis in solution, is stabilized in a quite remarkable crystalline arrangement that is suggestive of (1) a marked preference for uninhibited Mo=O double bonding in the complex anion and (2) a general mechanism whereby dehydrative hydrolysis of the crystal can occur. The complexing bond lengths, Mo–C = 2.204 ± 0.013 and Mo=O = 1.834 ± 0.009 Å, are each "anomalously" long for the type in an octahedral complex; it is pointed out that a significant lengthening of the equilibrium bond lengths is rationally concomitant with the concentration of excessively large resultant charge within an unduly limited volume.

Among the earlier investigations of the cyano complexes of quadrivalent and quinquevalent molybdenum, that of Bucknall and Wardlaw[5] in 1927 was both comprehensive and critical. Although they emphasized that the evidence developed during their study does not yield a unique formulation for the complex anion present in the red crystalline salt of empirical composition $4KCN \cdot MoO_2 \cdot 6H_2O$, most investigators, before and since, have favored the eight-coordinate formulation, $Mo(OH)_4(CN)_4^{4-}$, because the complex is readily derived from, or converted into, either of the octacyanomolybdate species, $Mo(CN)_8^{4-}$ or $Mo(CN)_8^{3-}$. On taking the red complex to be the $Mo(OH)_4(CN)_4^{4-}$ ion, it is then natural,[5] if by no means required, to write the blue hydrolytic product thereof as $Mo(OH)_3OH_2(CN)_4^{3-}$. Both species, if correctly formulated, would be especially pertinent to considerations of structure and bonding in discrete eight-coordination complexes.[6,7]

Quite recently, however, Lippard, *et al.*,[8,9] have presented a variety of persuasive, if somewhat indirect, evidence that the red complex present in the potassium and sodium salts is not the presumed $Mo(OH)_4(CN)_4^{4-}$ ion of the older literature, but is instead the *trans* form of the octahedral $MoO_2(CN)_4^{4-}$ ion. Our own X-ray examination of the potassium salt confirms the two-molecule monoclinic cell and the probable space group, $P2_1/c$-C_{2h}^5, reported by Lippard, *et al.*, and we agree that these data are incompatible with the existence in the crystal of $Mo(OH)_4(CN)_4^{4-}$ ions utilizing either of the coordination polyhedra that are known to be preferred for discrete eight-coordination.[7] The spectroscopic and other evidence which Lippard, *et al.*, educe in favor of the $MoO_2(CN)_4^{4-}$ formulation for the red complex (and of $MoO(OH)(CN)_4^{3-}$ for the blue species) need not be recapitulated here; we report instead a determination of structure for red orthorhombic crystals of a salt that is shown by our analysis to be correctly formulated as $NaK_3[MoO_2(CN)_4] \cdot 6H_2O$. Crystals of this mixed salt, identified as a minor impurity

---

[1] This investigation was supported in part by National Science Foundation Grant GP-6710X, by Public Health Research Grant No. 2-RO1 GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

[2] Presented in part at the Summer Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 20–25, 1967, Abstract P5, and in the Symposium on Unusual Coordination Polyhedra, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1967.

[3] National Science Foundation Predoctoral Trainee, 1965–1968.

[4] Author to whom correspondence should be addressed.

[5] W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927), who cite numerous references to earlier work in this field.

[6] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

[7] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

[8] S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967).

[9] S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **6**, 1943 (1967).

phase in preparations kindly supplied by Professor R. J. Archer of the potassium salt, were preferred for detailed analysis, in part because of their superior resistance to deterioration in the X-ray beam and to hydrolysis upon exposure to the atmosphere, but also for the more cogent reason discussed in the following section.

Both the easily hydrolyzed red complex and the blue hydrolytic product thereof are readily converted into the familiar stable octacyanomolybdate(IV) species by reaction with potassium cyanide.[5] Comparisons of the structural results obtained in this investigation with those recently reported for the octacyanomolybdate(IV) ion[10] prove to be quite illuminating in this connection.

Experimental Section

Two crystalline preparations of the red potassium salt, both maintained under ether in stoppered bottles to protect them from hydrolysis, were provided by Professor Archer. The selection by rapid visual inspection of crystal specimens that appeared to be particularly suitable for X-ray examination led, in a disproportionately large number of cases, to orthorhombic crystals of the impurity phase. Identification of the orthorhombic phase as $NaK_3MoO_2(CN)_4 \cdot 6H_2O$ crystallizing in a compact ordered structure was provided by the subsequent structure determination. Evidence that the proportion of the orthorhombic phase in the original preparation was small—about that anticipated from the fact that the ACS-approved KCN employed was allowed to contain 0.5% by weight of Na^+—was provided by an experiment performed (albeit inadvertently) toward the end of the study. Faulty stoppering of the bottle containing one preparation allowed the ether to escape and decomposition of the monoclinic potassium salt to proceed through the blue hydrolytic stage to white products, but within the white mass thus obtained were occasional orthorhombic crystals that had become superficially blue while retaining red cores. Indeed, the greater instability of the potassium salt was generally evidenced during the handling of specimen crystals. All X-ray study of either salt utilized single crystals sealed within thin-walled capillaries.

The orthorhombic unit cell of $NaK_3MoO_2(CN)_4 \cdot 6H_2O$, as determined by Weissenberg and precession techniques, has $a = 12.460 \pm 0.013$, $b = 7.161 \pm 0.008$, $c = 9.171 \pm 0.015$ Å; it contains two formula weights to give a calculated density of 1.95 g/cc, quite comparable with the 1.95 g/cc measured for the potassium salt[8] carrying the same water content. The systematically absent spectra are characteristic for the space group[11] Pmna-D_{2h}^7 and P2na (or Pnc2)-C_{2v}^6, of which the latter could permit $Mo(OH)_4(CN)_4^{4-}$ ions in either dodecahedral or antiprismatic configuration to exist within the crystal; less probable stereochemical forms of an eight-coordinate $Mo(OH)_4(CN)_4^{4-}$ would, of course, be compatible with either of these space groups and, indeed, with the two-molecule unit and probable space group ($P2_1/c$) of the potassium salt. The negative results of sensitive tests for piezoelectricity that were performed on a portion of the two-phase preparation as received lent support to the choice of a centrosymmetric space group for the monoclinic potassium salt, but were less convincing in their application to the occasional crystals of the orthorhombic phase that were randomly distributed within the mixture. The apparently wider range of structural possibilities afforded by the orthorhombic salt made it the choice for structure determination, and most of the required intensity data were recorded prior to the appearance of the Lippard, *et al.*, communication.[8]

Intensity data were photographically recorded on multiple films with filtered Mo Kα radiation from a crystal cut to the dimensions 0.275 × 0.225 × 0.15 mm. Eighteen layers of equiinclination Weissenberg data, recorded with rotation about the long axis of the specimen (and of the unit cell), together with two sets of precession data employed for correlative purposes provided nonvanishing intensities for 931 independent reflections, approximately the number comprised within the Cu Kα limiting sphere. With a linear absorption coefficient of 1.57 mm^{-1} for Mo Kα radiation and the experimental technique that was employed, the maximum variation of absorption in the specimen from the mean for the recorded reflections was approximately ±9%; the corrections for variable absorption that would have given a small, but probably significant, statistical improvement in the quality of the intensity data were not made. Intensities were visually estimated with the aid of carefully calibrated scales and were reduced to relative squared amplitudes, $|F|^2$, by means of the standard Lorentz and polarization factors. Numerous correlations among the several layers of Weissenberg data were made feasible by the precession data; scaling factors for individual layers were evaluated at this stage of the study and were not treated as disposable parameters during the subsequent determination and refinement of structure.

Structure determination was achieved through a combination of the heavy-atom technique, Fourier and difference syntheses, and least-squares refinement. The structure analysis, beginning with the three-dimensional Patterson synthesis, proved to be compatible at every stage and in all details with the requirements of the centrosymmetric Pmna; at no stage was there any hint that the complex anion could be other than the octahedral $MoO_2(CN)_4^{4-}$. A required feature of the analysis was the placement of most of the atoms (apart from hydrogen) in specialized positions that, in Pmna, are provided by symmetry considerations, but, in P2na, represent fortuitously specialized values for several of the atomic coordinates. Anisotropic full-matrix least-squares refinement[12,13] of the atomic arrangement based upon Pmna, including corrections for anomalous dispersion[14] in the form factor for molybdenum, led to a conventional R of 0.078 and a weighted R of 0.087 for the 931 independent reflections.[15] (Attempts at refinement based upon P2na were in all cases singularly unsuccessful.) The atomic coordinates and the thermal parameters thus derived, along with their estimated standard deviations, are listed in Tables I and II.

Table I. Atomic Coordinates in Crystalline $Na_3KMoO_2(CN)_4 \cdot 6H_2O$

Atom type	Site symmetry	Coordinates with standard deviations[a] 10^4x	10^4y	10^4z
Mo	C_{2h}-2/m	0	0	0
O	C_s-m	0	7926 (12)	1174 (12)
C_1	C_s-m	0	1820 (18)	1959 (14)
N_1	C_s-m	0	2818 (17)	2942 (13)
C_2	C_2-2	1758 (10)	0	0
N_2	C_2-2	2710 (8)	0	0
Na	C_{2h}-2/m	0	5000	5000
K_1	C_{2h}-2/m	0	0	5000
K_2	C_2-2	2500	3547 (5)	2500
w_s[b]	C_2-2	1459 (8)	5000	0
w_g[b]	C_1-1	1250 (6)	6781 (12)	3489 (9)

[a] Estimated standard deviations are given in parentheses. Coordinates listed without standard deviations are symmetry required. [b] Symbols used for water molecules in, respectively, special and general positions.

The Crystalline Arrangement

It is seen (Table I) that eight oxygen atoms of water molecules (and all hydrogen atoms) in the crystalline arrangement occupy eightfold general positions[11] of

---

(10) J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Am. Chem. Soc.*, **90**, 3177 (1968).

(11) "International Tables for X-Ray Crystallography," Vol. I. "Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, pp 141, 116, respectively.

(12) Slightly modified versions of the Busing–Martin–Levy ORFLS and ORFFE programs on a CDC 1604 computer were employed for final refinement. The data of Tables I and II and the cited R of 0.078 correspond to unit-weighting of all observed reflections. Modest changes in the weighting scheme have no objectively significant effect on the structural parameters

(13) Atomic form factors were from D. T. Cromer and J. T. Waber, *Acta Cryst.*, 18, 104 (1965).

(14) Dispersion corrections were those of D. H. Templeton in "International Tables for X-ray Crystallography," Vol. III, "Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962, pp 213–215.

(15) A table of observed and calculated structure amplitudes has been deposited as Document No. 9848 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

Table II. Anisotropic Thermal Parameters in Crystalline $NaK_3MoO_2(CN_4)\cdot 6H_2O$

Atom type	Thermal parameters, Å², with standard deviations[a] B_{11}	B_{22}	B_{33}	B_{23}
Mo	0.4 (0.04)	0.5 (0.04)	0.9 (0.04)	0.1 (0.1)
O	1.6 (0.3)	0.7 (0.3)	2.2 (0.4)	0.4 (0.3)
C_1	1.7 (0.5)	1.3 (0.5)	0.7 (0.4)	0.4 (0.4)
N_1	4.2 (0.7)	0.8 (0.4)	1.4 (0.4)	−0.1 (0.3)
C_2	1.3 (0.4)	2.0 (0.4)	2.5 (0.5)	−0.1 (0.9)
N_2	0.1 (0.4)	4.2 (0.6)	7.6 (1.0)	0.8 (1.1)
Na	1.8 (0.3)	1.1 (0.2)	1.8 (0.3)	−0.7 (0.4)
K_1	1.8 (0.1)	1.3 (0.1)	3.8 (0.2)	1.3 (0.3)
K_2	1.9 (0.1)	2.0 (0.1)	2.8 (0.1)	[b]
w_s[c]	2.0 (0.3)	2.0 (0.3)	2.2 (0.3)	0.2 (0.5)
w_g[c,d]	2.1 (0.3)	2.9 (0.3)	2.6 (0.3)	0.2 (0.3)

[a] Estimated standard deviations are the values in parentheses. [b] $B_{23} = 0$, but $B_{13} = -0.3$ (0.1). [c] Symbols used for water molecules as identified in Table I. [d] For w_g, $B_{12} = -0.6$ (0.3) and $B_{13} = -0.2$ (0.3).

Table III. Interatomic Distances and Angles in $NaK_3MoO_2(CN)_4\cdot 6H_2O$

		Interatomic Distances,[a] Å			
Mo—O	1.834 (9)	C_1—O	2.879 (18)	K_1—N_2	2.853 (10)
Mo—C_1	2.220 (13)	C_1—O′	2.880 (16)	K_1—C_1	3.087 (12)
$C_1 \equiv N_1$	1.150 (17)	C_2—O	2.857 (11)	K_1—w_g	3.108 (8)
Mo—N_1	3.369 (12)	Na—N_1	2.450 (12)	K_2—w_s	2.832 (5)
Mo—C_2	2.189 (12)	Na—w_g	2.444 (8)	K_2—w_g	2.935 (9)
$C_2 \equiv N_2$	1.186 (16)	w_g—O	2.758 (12)	K_2—N_1	3.184 (8)
Mo—N_2	3.375 (10)	w_g—N_2	2.985 (9)	w_s—O	2.976 (10)
C_1—C_2	3.118 (13)	K_1—N_1	2.763 (12)	w_s—w_g	3.420 (16)
		Angles,[b] Degrees			
MoC_1N_1	177.6 (1.1)	Ow_gN_2	111.8 (0.5)	w_gNaw_g	101.0 (0.4)
$OMoC_1$	90.0 (0.5)	Ow_gNa	103.6 (0.3)	w_gNaw_g'	79.0 (0.4)
C_1N_1Na	178.8 (1.1)	N_2w_gNa	114.6 (0.5)	w_gNaN_1	95.9 (0.3)
w_gOw_g'	68.6 (0.4)	$w_gN_2w_g'$	128.7 (0.5)	w_gNaN_1'	84.1 (0.3)

[a] Figures in parentheses are the estimated standard deviations in units of 10^{-3} Å. [b] Figures in parentheses are the estimated standard deviations.

Pmna: $\pm(x, y, z)$; $\pm(\bar{x}, y, z)$; $\pm(^1/_2 - x, y, {}^1/_2 - z)$; $\pm(^1/_2 + x, y, {}^1/_2 - z)$. Molybdenum atoms, sodium ions, and one-third of the potassium ions occupy sets of twofold positions having C_{2h}-2/m symmetry; the remaining atoms occupy fourfold positions having either C_2-2 or C_s-m symmetry. Although the structural grouping of greatest chemical interest is the octahedral *trans*-$MoO_2(CN)_4{}^{4-}$ ion, with the site symmetry of C_{2h} (and the effective symmetry of D_{4h}), it is preferable first to discuss the special role played by the sodium ions and the water molecules of w_g type in stabilizing the crystalline arrangement. Pertinent bond data are listed in Table III.

The sodium ion at 0, $^1/_2$, $^1/_2$ (Table I) coordinates four water molecules (w_g) occupying general positions and two nitrogen atoms of N_1 type, all in agreement with the site symmetry of C_{2h}, to give the octahedral grouping illustrated in Figure 1. Identification of the cations in the positions 2(c),[11] 0, $^1/_2$, $^1/_2$, and $^1/_2$, $^1/_2$, 0, as Na^+ rather than K^+, required initially by the difference syntheses, is fully confirmed by the observed values of the bond parameters in the octahedral $Na(OH_2)_4N_2$ grouping. Thus Na–w_g = 2.444 (0.008)[16] and Na–N_1 = 2.450 (0.012) Å, each more than 0.30 Å shorter than any analogous K–OH_2 or K–N separation observed either in this study or in the structure of crystalline $K_4Mo(CN)_8\cdot 2H_2O$.[10] The virtually linear array, –Mo–C_1–N_1–Na–, along one diagonal of the cell face lying in the mirror plane at $x = 0$ (Figure 1) is evidently conducive to strong Na–N_1 bonds. Although the Na–N_1 and Na–w_g bonds are of substantially equal length, the octahedral coordination group departs markedly from dimensional regularity: N_1-Naw_g angles are 84.1 and 95.9° (0.3°),[16] and w_g-Naw_g angles are 79.0 and 101.0° (0.4°). This distortion notwithstanding, the shortest w_g–w_g separation, 3.11 Å, is still ~0.31 Å longer than the van der Waals diameter of oxygen, and the shorter of the two N–w_g separations, 3.28 Å, is ~0.38 Å longer than the sum of the van der Waals radii for nitrogen and oxygen.[17]

Each water molecule of w_g type, moreover, is favorably placed (Figure 1) for simultaneous hydrogen bonding at 2.758 (0.012) Å with an oxygen atom of the complex anion and, less strongly, at 2.985 (0.009) Å with a nitrogen atom, N_2, lying on a twofold axis coincident with (or parallel to) *a*. Pertinent angles in this connection are: N_2w_gO, 111.8° (0.5°); Naw_gO, 103.6° (0.3°); Naw_gN_2, 114.6° (0.5°); w_gOw_g', 68.6° (0.4°); and $w_gN_2w_g'$, 128.7° (0.5°), wherein w_g' is related to w_g by reflection through $x = 0$. We further note that each w_g molecule is coordinated at 2.935 (0.009) Å to a potassium ion of K_2 type and, quite weakly, at 3.108 (0.009) Å to a potassium ion of K_1 type (Table I).

The close neighbors of the $K_1{}^+$ ion centered at 0, 0, $^1/_2$, a position of 2/m symmetry, are two N_1 atoms in the mirror plane (Figure 1) and two N_2 atoms on the twofold axis at $\pm x$, 0, $^1/_2$; the four nitrogen atoms delineate a nearly square rhombus in which the potassium ion is centered with K_1–N_1 = 2.763 (0.012) and K_1–N_2 = 2.853 (0.010) Å. The remainder of the coordination group corresponds to weak interactions; two C_1 atoms at 3.087 (0.012) and four w_g molecules at 3.108 (0.008) Å complete the coordination polyhedron around the potassium ion of K_1 type.

Two-thirds of the potassium ions are of K_2 type, positioned on twofold axes (Table I). Each $K_2{}^+$ ion has as relatively close neighbors two water molecules, w_s, at 2.832 (0.005) Å, two water molecules, w_g, at 2.935 (0.009) Å, and two nitrogen atoms, N_1, at 3.184 (0.008) Å; the next nearest neighbors are two carbon

---

(16) The figure given in parentheses following the value of a bond length or angle is the estimated standard deviation.

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

atoms at 3.39 Å. Each w_s molecule, moreover, is tightly coordinated only to two K_2^+ ions at the 2.832-Å distance noted above; other neighbors of a w_s molecule are two oxygen atoms of the complex anion at 2.976 (0.010) Å, and two w_g molecules at 3.42 Å. The structural efficiency with which each of the several types of cations and water molecules is employed may be briefly characterized as follows. Sodium ions, in the closest cooperation with the w_g water molecules, are employed to particular advantage, not only to stabilize the crystalline framework, but also (*vide infra*) to give the complex anions a comparatively large resistance to hydrolysis. Potassium ions of K_1 type are used primarily for direct bonding to nitrogen atoms; the four bonds from each K_1^+ ion together with the two bonds to N_1 atoms from each Na^+ ion are quite effective in tying the complex anions into a three-dimensional framework. The more numerous potassium ions of K_2 type and the w_s water molecules are used, individually with low structural efficiency, to fill out and further stabilize the primary framework. We remark, in this connection, that the stoichiometry of such crystalline salts as $K_4Mo(CN)_8 \cdot 2H_2O$[10] and, presumably, $K_4MoO_2(CN)_4 \cdot 6H_2O$ requires most or all of the univalent cations to accept structural environments that are far from ideal. The partial substitution of sodium for potassium ions introduces new degrees of freedom that, as exemplified by the structure of $NaK_3MoO_2(CN)_4 \cdot 6H_2O$, may lead to improved structural relations.

The $MoO_2(CN)_4^{4-}$ Ion. The octahedral $MoO_2(CN)_4^{4-}$ ion, with the required symmetry of C_{2h}-2/m, has two cyanide ligands of type 2 extending along the twofold axis and the four remaining ligands centered in the mirror plane (Figure 1). The only bond angles that are not fixed by symmetry lie in the mirror plane; these are $OMoC_1 = 90.0°$ (0.5°) and $MoC_1N_1 = 177.6°$ (1.1°). The Mo–O distance, 1.834 (0.009) Å, is strongly suggestive of double bonding. The two independently determined Mo–C distances, 2.220 (0.013) and 2.189 (0.012) Å, average to 2.205 Å; the two C≡N distances, 1.150 (0.017) and 1.186 (0.016) Å, average to 1.168 Å; and the two MoCN chain lengths, 3.369 (0.012) and 3.375 (0.010) Å, average to 3.372 Å. It is seen, consequently, that the deviation from the average for the type is in no case objectively significant. Furthermore, the assignment of effective D_{4h}-4/mm symmetry to the complex anion is evidently justified.

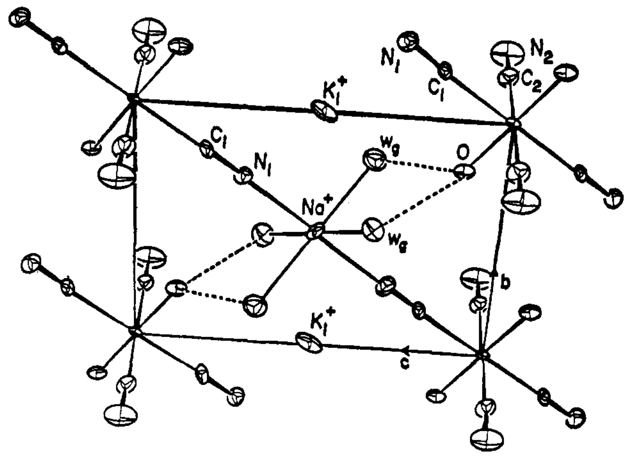

Figure 1. Partial diagram in perspective of the crystalline arrangement that includes the atoms centered in and near the plane, $x = 0$. Solid lines are used to depict the bonding patterns within the $MoO_2(CN)_4^{4-}$ complexes located at cell vertices and within the octahedral coordination group of the sodium ion centered at 0, 1/2, 1/2. Broken lines depict the short hydrogen bonds formed by oxide oxygen atoms of the anion with w_g water molecules. The near neighbors of the K_1^+ ion centered at 0, 0, 1/2 are two N_1 atoms in $x = 0$ (as shown) and two N_2 atoms above and below at $\pm x$, 0, 1/2. The ellipsoidal shapes representing atoms in the diagram are indicative of the relative strengths and anisotropies of the thermal motions.

Taking the M–O bonds along $\pm z$ and the MoCN chains along $\pm x$ and $\pm y$ in a D_{4h} description of the diamagnetic[9] d^2 $MoO_2(CN)_4^{4-}$ complex, the assignment of the $4d_{z^2}$, $4d_{x^2-y^2}$, and 5 sp^3 orbitals in the valence shell of the Mo(IV) atom to σ bonding is straightforward. The relatively very short Mo–O bond distance then suggests that the degenerate pair of d orbitals, d_{yz} and d_{zx}, are fully employed in "forward" π bonding with the two oxide oxygen atoms. The concomitant housing of the quasi-inert electron pair in the most stable d_{xy} orbital is conducive, at least in principle, to some measure of "back" π bonding with the four cyanide ligands. A generally analogous possibility for such back π bonding with the four cyanide ligands of the B type[7] exists also in the d^2 $Mo(CN)_8^{4-}$ ion, the otherwise distinctive geometry and pattern of σ bonding in this dodecahedral complex notwithstanding. Indeed, it is quite illuminating to compare bond lengths within the MoCN chains of the octahedral $MoO_2(CN)_4^{4-}$ ion with those recently reported[10] for the eight-coordinate $Mo(CN)_8^{4-}$ species as this exists in orthorhombic crystals of $K_4Mo(CN)_8 \cdot 2H_2O$.

The averaged values,[18] with accompanying mean deviations from the average, that are reported[10] for distances in the MoCN chains of the $Mo(CN)_8^{4-}$ complex are: Mo—C, 2.163 ± 0.005; C≡N, 1.152 ± 0.006; and Mo—N, 3.314 ± 0.008 Å. The corresponding estimated standard deviations for the individual distances of each class are, respectively, 0.007, 0.009, and 0.008 Å. (We note that these data afford no dimensional basis for distinguishing between bonds of the A and B types.[10])

The MoCN chain length (or Mo–N distance) of 3.772 Å in the $MoO_2(CN)_4^{4-}$ ion is longer by an objectively significant 0.058 Å than the chain length of 3.314 Å in the $Mo(CN)_8^{4-}$ complex. The larger part, but probably not all, of this increase in chain length appears in the longer Mo–C bond length that characterizes the octahedral complex. Although the accompanying apparent increase of 0.016 Å in the C≡N distance does not meet objective tests for significance, a modest increase in this bond length is perhaps consistent with reported values of the infrared C≡N stretching frequencies in the complex anions. Thus the $Mo(CN)_8^{4-}$ ion, under the site symmetry of C_s-m in crystalline $K_4Mo(CN)_8 \cdot 2H_2O$, gives C≡N stretching frequencies distributed within the range[19] from 2103 to 2136 cm^{-1} and, in aqueous solution (probably as an antiprismatic species[10]), just one well-defined stretching frequency[19] at 2111 cm^{-1}. The $MoO_2(CN)_4^{4-}$ ion, in crystals of

---

[18] The value given for each distance is the average of six independently determined quantities corresponding to the fact that the $K_4Mo(CN)_8 \cdot 2H_2O$ structure carries six symmetry-nonequivalent classes of MoCN chains.

[19] S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, 21, 1087 (1965).

the sodium and the potassium salts, is reported[9] to give in each case a single C≡N stretching frequency (as if the site symmetry were D_{4h}) at 2075 or 2060 cm^{-1} respectively in the sodium or the potassium salt. (The $MoO_2(CN)_4{}^{4-}$ ion, upon solution, is hydrolyzed to the blue species, $MoO(OH)(CN)_4{}^{3-}$, as formulated by Lippard, *et al.* The C≡N stretching frequencies in the blue complex are apparently intermediate between those of the $MoO_2(CN)_4{}^{4-}$ and the $Mo(CN)_8{}^{4-}$ species.[9]) The smaller force constant concomitant with the lower stretching frequency of the C≡N bonds in the $MoO_2(CN)_4{}^{4-}$ ion is likely to be coupled with a slightly longer C≡N bond length than that which characterizes the $Mo(CN)_8{}^{4-}$ species.

The data cited for the Mo–C bonds in the $MoO_2(CN)_4{}^{4-}$ and $Mo(CN)_8{}^{4-}$ complexes are clearly in marked disagreement with the general rule that an increase in coordination number from six (octahedral) to eight implies an increase of 3–5% in the length of the complexing bonds. Consideration of the bonding problem, as detailed below, leads to the identification of a critical (if customarily neglected) feature of the bonding that can plausibly account for the observation that the Mo–C bonds are longer in the more compact, geometrically simpler, octahedral complex.

The tight packing of the ligands in the $Mo(CN)_8{}^{4-}$ ion gives rise to a destabilizing energy term associated with the closed-shell repulsions that may well be of the order of 50 kcal/mole,[7,10] whereas the corresponding energy term in the octahedral $MoO_2(CN)_4{}^{4-}$ ion is, by comparison, rather unimportant; it is clear that the nonbonding repulsions of this type are (as always) conducive to longer complexing bonds in the eight-coordinate complex.

It may then seem that the inward transfer of charge associated with the highly developed Mo–O π bonding in the $MoO_2(CN)_4{}^{4-}$ species should encourage the outward charge transfer associated with the Mo–CN π bonding beyond that which characterizes the $Mo(CN)_8{}^{4-}$ complex. Such enhancement of the back π bonding does provide a possible (but not unique) explanation of the lower C≡N stretching frequency observed in the octahedral complex; the concomitant contribution to a tightening of the complexing Mo–CN bonds is, if present, wholly obscured in the observed increase in the Mo–C distance that must be ascribed to some other more influential source. It seems, indeed, that back π bonding in the d^2 Mo(IV) complexes under scrutiny plays an altogether less important role than does forward π bonding in the dodecahedral d^0 oxozirconate(IV) species.[10,20,21]

It is quite improbable that the shorter bond lengths in the MoCN chains in the $Mo(CN)_8{}^{4-}$ ion are ascribable to the use in σ bonding of two d orbitals (d_{yz} and d_{zx}) of the Mo(IV) atom in addition to the d^2sp^3 set specified earlier for the octahedral $MoO_2(CN)_4{}^{4-}$ species; similar patterns for σ bonding characterize the oxozirconate(IV) complexes which exhibit the expected increase in the averaged bond length[21] with increase in coordination number.

The paucity, especially in solution, of stable quadruply charged species that consist each of just a few atoms in a compact grouping directs attention to the destabilizing Coulombic energy associated in such species with any plausible distribution of the very large resultant charge. Short of a fundamental quantum mechanical discussion that would eliminate the need for piecemeal discussion of the bonding, we lack means for determining the distribution of resultant charge. If, however, we assign one electronic unit, e, of charge to each oxygen atom in the $MoO_2(CN)_4{}^{4-}$ ion, e/2 to each nitrogen atom in both complexes, and use the observed distances in computing formal Coulomb energies, we obtain 528 kcal/mole for the $MoO_2(CN)_4{}^{4-}$ ion and either 493 or 484 kcal/mole for $Mo(CN)_8{}^{4-}$ accordingly as we use the Mo–N distance (3.314 Å) observed in this complex or that (3.372 Å) from the octahedral species. A symmetrical shrinking of 5% in the observed dimensions of the $MoO_2(CN)_4{}^{4-}$ species, corresponding to a 3% shortening of the MoCN chain length from the 3.314 Å in $Mo(CN)_8{}^{4-}$, gives a computed Coulomb energy of 555 kcal/mole, 62 kcal/mole larger than for the $Mo(CN)_8{}^{4-}$ ion; the shrunken value of the Mo–O distance, 1.74 Å, is then comparable with the 1.736 ± 0.005 Å observed for the Mo(VI)=O double bond in the MoO_3 moiety as this is stabilized, with the Mo(VI) atom in quasi-octahedral coordination, by comparatively weak complexing with either diethylenetriamine[22] or with (half of) an ethylenediaminetetraacetate ion.[23]

The import of these computations is not only to suggest the obvious fact that large resultant charge is strongly destabilizing, but also to suggest that such charge must lead to significantly longer than normal values of the equilibrium bond lengths. Although the true lengthening of the complexing bonds produced by the Coulombic repulsions is not calculable, its importance is scarcely in question; the Mo–C bond lengths in the two Mo(IV) complexes appear to illustrate the differential lengthening produced by Coulombic repulsions of substantially different magnitudes. The greater length, 1.83 Å, of the Mo–O bond in $MoO_2(CN)_4{}^{4-}$ relative to the 1.74 Å cited for the MoO_3 moiety probably is not solely attributable to the large resultant charge, inasmuch as the presence of the quasi-inert electron pair in the d_{xy} orbital of the central atom presumably inhibits to some degree the inward transfer of charge associated with the multiple Mo–O bonding. Both effects, however, are included in the qualitative conclusion that the lengthened bond is the result of concentrating overmuch charge within a limited volume.

Comparing the red $MoO_2(CN)_4{}^{4-}$ and the blue $MoO(OH)(CN)_4{}^{3-}$ ions,[9] it is only the blue species that is important in aqueous solution excepting, possibly, at extremely high pH. At low pH the blue complex is transformed into a less fully characterized green species to which the straightforward, if somewhat tentative,

---

[20] J. L. Hoard, E. W. Silverton, and J. V. Silverton, *J. Am. Chem. Soc.*, **90**, 2300 (1968).

[21] In a dodecahedral ZrO_8 coordination group, the complexing bond lengths of A and B types are expected to differ[20] by ~0.10 Å. This difference, by comparison with the lack thereof in the $Mo(CN)_8{}^{4-}$ ions, is directly indicative of the relative benefits from forward and back π bonding.[10,20] In both antiprismatic and dodecahedral ZrO_8 coordination groups, the averaged Zr–O bond distance lies in the range 2.19–2.20 Å.

[22] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 3, 397 (1964); F. A. Cotton and R. M. Wing, *ibid.*, 4, 867 (1965). The three Mo–N complexing bonds have an average length of 2.324 Å.

[23] M. D. Glick, J. J. Park, and J. L. Hoard, "Proceedings of the Ninth International Conference on Coordination Chemistry," St. Moritz-Bad, Switzerland, Sept 5–9, 1966, p 424. The lengths of the additional complexing bonds to each Mo(VI) atom in the binuclear complex are 2.396 Å for Mo–N and 2.190 Å as the average for Mo–O.

formula $Mo(OH)_2(CN)_4^{2-}$ has been assigned.[9] The red complex affords the minimum of constraints on Mo–O multiple bonding, but with the concomitant liability of a resultant charge so large as to require the species to be stabilized in the ordered positive field provided by the cations in a crystalline arrangement.[24] The decided preference of the Mo(IV) and oxide oxygen atoms for uninhibited double bonding is most clearly suggested by one outstanding feature of the crystalline structure of $NaK_3MoO_2(CN)_4 \cdot 6H_2O$. Each oxygen atom of the complex anion is strongly hydrogen-bonded to two (w_g) water molecules of the partially hydrated sodium ion so that the transfer of any one of four protons from a w_g molecule to a complexed oxygen atom, a jump of only 0.70 Å for the proton, would transform the red $MoO_2(CN)_4^{4-}$ into the blue $MoO(OH)(CN)_4^{3-}$ species. Although a statistical distribution of the protons between the two classes of positions thus defined would contribute entropic stabilization without detriment to the structural integrity of the arrangement, it appears that a fully ordered structure is required by energetic considerations in which Mo=O double bonding plays a critical role.

Partial collapse of the crystalline arrangement, engendered by the loss of the weakly held water molecules of w_s type (*vide supra*), presumably would stimulate proton transfer from the w_g water molecules to the complex anion and thus provide a general mechanism for dehydrative hydrolysis—a phenomenon reported for crystals of the potassium salt when these are maintained in a desiccator over concentrated sulfuric acid.[5,9] The precise course and the final products of such dehydrative hydrolysis of crystalline $K_4MoO_2(CN)_4 \cdot 6H_2O$ remain in doubt; the earlier study[5] specified a color change from red to blue, suggesting formation of the $MoO(OH)(CN)_4^{3-}$ species, whereas Lippard and Russ[9] report a dull green or yellow-green product that suggests the presence of the $Mo(OH)_2(CN)_4^{2-}$ species.

The structure determination detailed herein serves to underwrite, in large measure, the conclusions drawn by Lippard and Russ from their study of the oxocyano and hydroxocyano complexes of molybdenum(IV). Perhaps the most interesting conclusion, negative though it be, is that the "classical" eight-coordinate $Mo(OH)_4(CN)_4^{4-}$ complex is not a stable species either in crystalline phases or in aqueous solution. This instability is not primarily attributable to the steric limitations imposed by the geometry of eight-coordination, but seems rather to arise from the energetic preference for just two molybdenum–oxygen bonds carrying each the maximum bond order.

---

[24] A clear-cut example of excessive resultant charge producing instability in aqueous solution of a sterically excellent complex is provided by the octafluorotantalate(V) ion. The antiprismatic TaF_8^{3-} ion, with Ta–F ~ 1.98 Å, is stabilized by sodium ion in the excellent Na_3TaF_8 crystalline structure,[25] but it gives way completely in aqueous solution to the heptafluorotantalate(V) species,[26] TaF_7^{2-}, in a configuration[27] (C_{2v} monocapped trigonal-prismatic) that represents but little reduction in the closed-shell nonbonding interactions.

[25] J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *J. Am. Chem. Soc.*, 76, 3820 (1954).

[26] O. L. Keller and A. Chetham-Strode, *Inorg. Chem.*, **5**, 367 (1966).

[27] J. L. Hoard, *J. Am. Chem. Soc.*, 61, 1252 (1939).

Equilibria of Metal Ions with Pyrocatechol and 3,5-Di-*t*-butylpyrocatechol[1,2]

Charles A. Tyson and Arthur E. Martell[3]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois. *Received August 7, 1967*

Abstract: The equilibrium constants from the reaction of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions with pyrocatechol in aqueous solution, and with pyrocatechol and 3,5-di-*t*-butylpyrocatechol in 50% methanol, have been studied potentiometrically, and those obtainable by this method are reported. Ultraviolet spectra of the manganese(II)- and copper(II)-pyrocatechol systems are consistent with the aqueous equilibria determined potentiometrically involving the formation of 1:1 and 1:2 chelates. The first protonation constant of pyrocatechol is determined more accurately than has previously been reported, resulting in the calculation of better values of the corresponding metal chelate formation constants. Differences in the nature of the complexes formed in 50% methanol, and the lower rate of complex formation, are ascribed to the greater basicity of the mixed solvent. Explanations are offered for the variety of metal ion complexes formed with 3,5-di-*t*-butylpyrocatechol. The results obtained indicate that manganese 3,5-di-*t*-butylpyrocatechol may serve as a model for the study of pyrocatechol autoxidation mechanisms.

Preliminary to an investigation into the mechanism of the metal-catalyzed oxidation of pyrocatechols, equilibria were studied in aqueous and 50% methanol–water solvents for pyrocatechol and 3,5-di-*t*-butylpyrocatechol complexes of Zn(II) and of first-row transition metals. Previous work on equilibrium and stability constants for Cu^{2+}–,[4–9] Zn^{2+}–,[7] and Fe^{3+}–pyrocate-

---

[1] Abstracted in part from a thesis submitted to the Faculty of Illinois Institute of Technology in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] This work was supported by Research Grant No. WP-00744 from the Water Pollution Administration of the Department of the Interior.

[3] Department of Chemistry, Texas A&M University, College Station, Texas 77843.

[4] R. Nasanen and R. Markkanen, *Suomen Kemistilehti*, **29B**, 119 (1956).

[5] C. F. Timberlake, *J. Chem. Soc.*, 4987 (1957).