Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Structure of Tripotassium Octachloroditechnetate Hydrate

F. ALBERT COTTON* and LARRY W. SHIVE

Received January 2, 1975 AIC50005Z

The crystal structure of $K_3Tc_2Cl_8 \cdot nH_2O$ has been determined by X-ray crystallography. Data were refined in both of the possible space groups indicated by the systematic absences, $P3_121$ and $P3_221$; they were indistinguishable. The unit cell parameters are a = 12.838 (3) Å, c = 8.187 (2) Å, and V = 1168.4 (5) Å^3. The calculated density for Z = 3 and mol wt 633.11 is 2.70 g cm^{-3}. Mo Kα radiation, monochromatized by a graphite crystal, was used to collect data in the range $0° < 2\theta \leq 71°$. Refinement on the 64 variables using the 1402 reflections for which $I_o > 3\sigma(I_o)$ gave final R values of R_1 = 0.051 and R_2 = 0.063 for both space groups. The structure contains $Tc_2Cl_8^{3-}$ anions located on twofold axes. These anions have virtual D_{4h} symmetry and are similar in structure to the $Re_2Cl_8^{2-}$ anion. The Tc–Tc' distance is 2.117 (2) Å and the average Tc–Cl distance is 2.36 Å. The compound is isostructural with $(NH_4)_3Tc_2Cl_8 \cdot nH_2O$. The water content seems to approximate to $2H_2O$ although full occupancy of the crystallographic positions for the oxygen atoms would give the trihydrates.

Introduction

Shortly after the discovery[1] of the first quadruple bond, in the $Re_2Cl_8^{2-}$ ion, an interesting and important example of a deviation from the ideal $\sigma^2\pi^4\delta^2$ bonding configuration for such species was described. An X-ray crystallographic structure[2] of the compound $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$[3] revealed that its important component is the $Tc_2Cl_8^{3-}$ ion, a species in which there must be one electron outside of the $\sigma^2\pi^4\delta^2$ configuration.

One of the important questions which is still not conclusively resolved concerning quadruply bonded species is the ordering and provenance of the molecular orbitals lying above the δ orbital. It was proposed in early papers[1d,4] that there would be two σ-nonbonding levels (σ_n's) in the neighborhood of δ^* with one of them lying below it, i.e., between δ and δ^*. The provenance of these orbitals was assumed to be the metal s and p_z orbitals. Very recent SCF–SW–Xα calculations[5a,b] on $Mo_2Cl_8^{4-}$ as well as a more conventional MO calculation[5c] on $Tc_2Cl_8^{3-}$ and experimental measurements[6] on $Tc_2Cl_8^{3-}$ have not provided support for this positioning of the σ_n's although all of the other, essential features of the quadruple-bond scheme[1d] as originally proposed have been substantiated. The possible absence of low-lying σ_n's, according to the above calculations, might be attributed to the necessary parent atomic orbitals, s or p_z, or both, being of too high an energy to form MO's which would be found as far down in the MO diagram as the δ^* orbital. However, there still remains considerable uncertainty as to the details of bonding in these compounds.

It must be remembered, however, that even in the absence of the postulated virtual σ_n orbital in a species such as $Mo_2Cl_8^{4-}$ the possibility is not precluded that the additional electron in $Tc_2Cl_8^{3-}$ might occupy an orbital whose greatest amplitude is in those regions trans to the Tc–Tc bond, even if its provenance is not primarily in the s and p_z orbitals of the metal atom valence shells. The regions of space in question should be most favorable on the basis of interelectronic repulsions since all other regions (i.e., those between the metal atoms and the chlorine atoms and especially that between the metal atoms) are already occupied by bonding electrons.

Because the $Tc_2Cl_8^{3-}$ ion may well be a particularly informative subject for further studies of bonding and electronic structure of multiple metal–metal bonds, an accurate structural description of it is important. The previously reported structure was based on film data and gave the Tc–Tc bond length with an accuracy of only ±0.01 Å. Moreover, the cation NH_4^+ together with the water molecules formed a complex, hydrogen-bonded structure which was difficult to decipher. We had, therefore, decided to determine the $Tc_2Cl_8^{3-}$ structure more accurately employing an alkali metal salt.

It was therefore of particular interest when the preparation of compounds alledged to have the composition $M^I_8(Tc_2Cl_8)_3 \cdot 4H_2O$ with M^I = NH_4, K, or Cs was reported in 1973.[7] The formulas were said to be based on direct determination of the oxidation number of technetium as 2.62 for the K salt and 2.68 for the NH_4 salt. The authors also cited an X-ray crystallographic study[8] which, they said, showed that "technetium exists as a binuclear anionic octachloroditechnetate $[Tc_2Cl_8]_3^{8-}$ in which technetium has an average valence of 2.67". However, the X-ray study they cited actually reports that the K and Cs compounds have the formula $M^I_3[Tc_2Cl_8] \cdot 2H_2O$ and are isostructural with $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$. This study dealt principally with the potassium salt, but the results appeared to be of even poorer quality than those for the ammonium compound; the positions of the water oxygen atoms are not reported at all. We felt that a fresh structural study of one of the alkali salts was worthwhile not only to ascertain the Tc–Tc distance with greater precision but also to clarify many features left obscure by both of the previous studies.

Experimental Section

Yttrium octachloroditechnetate, YTc_2Cl_8, was prepared for us by Dr. E. Pedersen using literature procedures,[2,3] with slight modifications.[6a] An acid solution of YTc_2Cl_8 was saturated with KCl causing the precipitation of a gray-black solid. This was recrystallized from 6 N HCl by evaporation in a desiccator. Microscopic examination of the crystals revealed several that were suitable for X-ray diffraction studies. One of these with approximate dimensions of 0.23 × 0.11 × 0.07 mm was sealed in a glass capillary and placed on a goniometer head.

Crystallographic Procedures. Fifteen intense reflections from the crystal were automatically centered on a Syntex $P\bar{1}$ four-circle automatic diffractometer and were used in a least-squares refinement to calculate cell parameters and an orientation matrix. Peak width at half-height from ω scans of several of the most intense reflections was measured to be 0.2°. The trigonal cell parameters are a = 12.838 (3) Å, c = 8.187 (2) Å, and V = 1168.4 (5) Å^3. For Z = 3 and mol wt 633.11, the calculated density is 2.70 g cm^{-3}; the previously reported[8] measured density is 2.79 g cm^{-3}.

Data were collected at 23° using Mo Kα radiation with a graphite-crystal monochromator in the incident beam. The θ–2θ scan technique with scan rates varying from 4 to 24° min^{-1}, depending upon the reflection intensity, was used to collect 3357 reflections in the range $0° < 2\theta \leq 71°$. The scan range was from 0.9° below the Kα_1 peak to 0.9° above the Kα_2 peak. No significant change in intensities was noted for three reflections which were periodically monitored during data collection. Additional details of data collection have been given.[9] An absorption correction was applied to the data since the absorption coefficient is 38 cm^{-1} and the transmission factors varied from 0.609 to 0.820. The crystal was carefully measured on an optical goniometer. Programs for data reduction, absorption correction, and structure analysis are listed below.[10] After the absorption correction, a program was run to eliminate equivalent reflections. The reflections used in refinement were those with either $0 \leq h = k$, $l \geq 0$, or $0 < h < k$, all values of l. The data included 120 Friedel pairs.

Solution and Refinement of the Structure. The structure was solved

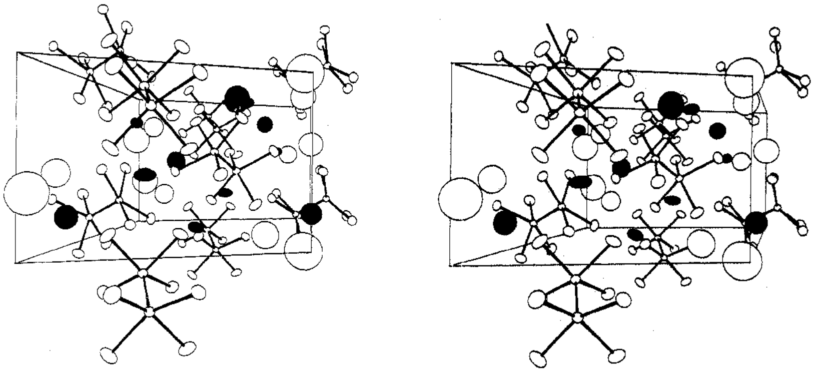

Figure 1. A stereoscopic ORTEP view of the unit cell in which atoms are represented by their ellipsoids of thermal vibration drawn to enclose 50% of their electron density. Dark ellipsoids represent potassium ions.

using the $P3_121$ space group. A three-dimensional Patterson map revealed the position of the heavy atom. This position was refined in two cycles of full-matrix least squares and gave residuals of $R_1 = (\sum \| F_o| - |F_c\|)/\sum|F_o| = 0.35$ and $R_2 = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.44$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is given by $4|F_o|^2/\sigma^2$ where σ is the esd of $|F_o|^2$. A difference electron density map revealed the positions of all the other atoms which were then included in the next three cycles of refinement. The multiplier of O(1) and the isotropic thermal parameter of K(2) were then refined holding all other variables constant. The multiplier of O(1) and the isotropic thermal parameters of K(2) and the oxygen atoms were then refined for two cycles to near convergence. Two final cycles involving anisotropic refinement of the technetium atom, four chlorine atoms, and one potassium atom and isotropic refinement of the other three atoms, gave final residuals of 0.051 and 0.063. The error in an observation of unit weight was 1.29.

The O(2) atom was found to be in a chemically unreasonable position with respect to O(1). However, when it was omitted, the error in an observation of unit weight and the R values increased 0.5%. It was then placed at a reasonable position suggested in a difference electron density map and again refined. It moved back to the unreasonable coordinates during refinement and was left there.

Two cycles of refinement in the enantiomorphic $P3_221$ space group using $-X$, $-Y$, $-Z$ positions from $P3_121$ gave the same residuals. A comparison of $F_{o_{hkl}}/F_{o_{\bar{h}\bar{k}\bar{l}}}$ vs. $F_{c_{hkl}}/F_{c_{\bar{h}\bar{k}\bar{l}}}$ was made in an attempt to determine the absolute configuration[11] of this structure. Completely random results were obtained which favored neither space group.

Next, two cycles of refinement in each space group were carried out in which the effects of anomalous scattering were not considered. No shift greater than 1 esd was observed for any of the positional parameters. The residuals were $R_1 = 5.1$ and $R_2 = 6.4$ and the error in an observation of unit weight increased slightly, to 1.31.

Only those 1402 reflections for which $I_o > 3\sigma(I_o)$ were used for final refinement of the 64 variables. A final difference electron density map did not reveal any hydrogen atom. Scattering factors of Cromer and Waber were used.[12] Anomalous scattering from Tc, K, and Cl atoms was included in calculations of F_c, with values from Cromer and Liberman.[13] No unusual trends were found in the values of $\sum w(|F_o| - |F_c|)^2$ as a function of Miller indices, classes of Miller indices, $\lambda^{-1} \sin \theta$, or $|F_o|$.

The observed and calculated structure factor amplitudes expressed as $10|F_o|$ and $10|F_c|$ are available.[14] Atomic positional parameters and anisotropic and isotropic thermal parameters for the $P3_221$ space group are listed in Tables I and II. Root-mean-square amplitudes of thermal vibration are in Table III.

Table I. Atomic Positional Parameters (Å)

Atom	x	y	z
Tc	−0.08283 (7)	−0.63814 (8)	−0.10291 (8)
Cl(1)	−0.0553 (3)	−0.7464 (4)	−0.8910 (4)
Cl(2)	−0.0597 (3)	−0.4994 (3)	−0.8940 (4)
Cl(3)	−0.2042 (3)	−0.5719 (3)	−0.2340 (3)
Cl(4)	−0.1998 (3)	−0.8198 (3)	−0.2435 (4)
K(1)	0.1843 (3)	−0.4863 (4)	0.2508 (3)
K(2)	0.0	−0.287 (1)	−0.166667
O(1)	−0.041 (3)	−0.183 (3)	0.094 (4)
O(2)	0.0	0.032[a]	0.333333

[a] See Experimental Section.

Table II

Anisotropic Temperature Factors[a] (×10⁴)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tc	27.5 (6)	32.8 (6)	45.8 (8)	13.3 (5)	0.4 (6)	2.4 (6)
Cl(1)	62 (3)	74 (3)	116 (4)	34 (2)	5 (3)	45 (3)
Cl(2)	47 (2)	65 (2)	83 (4)	16 (2)	6 (2)	−25 (2)
Cl(3)	42 (2)	70 (3)	92 (4)	33 (2)	2 (2)	17 (2)
Cl(4)	51 (2)	46 (2)	125 (4)	8 (2)	2 (3)	−19 (2)
K(1)	54 (2)	152 (5)	86 (4)	24 (3)	−6 (2)	−11 (3)

Isotropic Temperature Factors

Atom	B, Å²	Atom	B, Å²	Atom	B, Å²
K(2)	10.0 (3)	O(1)	12 (1)	O(2)	24 (2)

Occupancy Factor

O(1)	0.79 (5)

[a] These are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Root-Mean-Square Amplitudes of Thermal Vibration (Å)

Atom	Min	Intermed	Max
Tc	0.124 (1)	0.131 (1)	0.149 (1)
Cl(1)	0.140 (4)	0.195 (4)	0.257 (4)
Cl(2)	0.144 (4)	0.168 (4)	0.246 (4)
Cl(3)	0.145 (4)	0.168 (4)	0.220 (4)
Cl(4)	0.148 (4)	0.193 (4)	0.239 (6)
K(1)	0.166 (4)	0.188 (4)	0.344 (5)

Results and Discussion

The unit cell contains $Tc_2Cl_8^{3-}$ anions, potassium ions, and water molecules. The metal–metal bond in the $Tc_2Cl_8^{3-}$ ion is bisected by a crystallographic diad axis which also runs through the K(2) and O(2) atoms. No hydrogen atom positions were found for the disordered water molecules represented by O(1) and O(2). The occupancy factor for O(1) is 0.79 (5). A stereoview of the unit cell and its contents is shown in Figure 1. Figure 2 is a drawing of the $Tc_2Cl_8^{3-}$ ion.

Four chlorine atoms and one technetium atom compose the square-pyramidal coordination sphere of each Tc atom. A twofold axis is the only crystallographic symmetry of the $Tc_2Cl_8^{3-}$ ion which has virtual D_{4h} symmetry. The axial coordination site of each metal atom is vacant. A chlorine atom from another $Tc_2Cl_8^{3-}$ group is 3.579 (3) Å away with a Tc–Tc···Cl angle of 176°. This appears to be a normal, nonbonded contact. As in $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$,[2] the $Re_2Cl_8^{2-}$ ion,[15] and the $Mo_2Cl_8^{4-}$ ion[16] the chlorine atoms across the metal–metal bond are eclipsed and the distorted cube formed by the eight chlorine atoms has edge lengths in the 3.2–3.4-Å range. The Tc–Tc bond distance, 2.117 (2) Å, indicates a strong metal–metal bond. The average Tc–Cl distance is 2.36

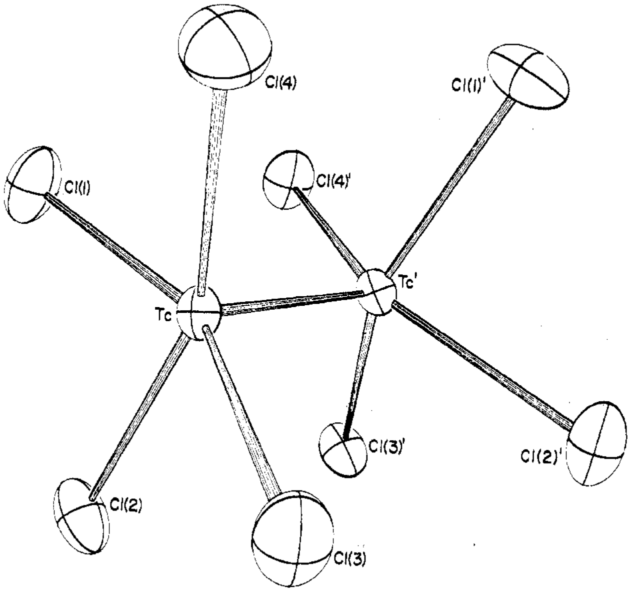

Figure 2. An ORTEP drawing of the $Tc_2Cl_8^{3-}$ anion, in which each atom is represented by its ellipsoid of thermal vibration at the 50% level. Atoms with "prime" designations are related to those without primes by a twofold axis.

Table IV. Interatomic Distances and Angles in $Tc_2Cl_8^{3-}$

Atoms	Bond dist, Å	Atoms	Bond dist, Å
Tc-Tc'	2.117 (2)	Tc-Cl(3)	2.372 (3)
Tc-Cl(1)	2.357 (3)	Tc-Cl(4)	2.348 (3)
Tc-Cl(2)	2.379 (3)		
Atoms	**Nonbonded dist, Å**	**Atoms**	**Nonbonded dist, Å**
Cl(1)···Cl(2)	3.200 (4)	Cl(1)···Cl(4)'	3.271 (5)
Cl(1)···Cl(4)	3.303 (4)	Cl(2)···Cl(3)'	3.382 (4)
Cl(2)···Cl(3)	3.214 (4)	Tc···Cl(3)	3.579 (3)
Cl(3)···Cl(4)	3.212 (4)		
Atoms	**Bond angle, deg**	**Atoms**	**Bond angle, deg**
Tc'-Tc-Cl(1)	104.48 (9)	Cl(1)-Tc-Cl(3)	150.0 (1)
Tc'-Tc-Cl(2)	105.11 (8)	Cl(1)-Tc-Cl(4)	89.1 (1)
Tc'-Tc-Cl(3)	105.77 (7)	Cl(2)-Tc-Cl(3)	85.1 (1)
Tc'-Tc-Cl(4)	103.89 (8)	Cl(2)-Tc-Cl(4)	151.0 (1)
Cl(1)-Tc-Cl(2)	85.0 (1)	Cl(3)-Tc-Cl(4)	85.7 (1)

Å. Interatomic distances and angles for the $Tc_2Cl_8^{3-}$ ion are listed in Table IV.

Each potassium atom is located above a plane of four chlorine atoms which constitute a face of the $Tc_2Cl_8^{3-}$ cube. Table V lists these contact distances along with other K···Cl contact distances. It will be noted that K(1) is more tightly enclosed in a coordination sphere than is K(2); this is reflected in a comparison of thermal parameters for the two atoms.

The poor behavior of the two water molecules during refinement indicates that they are held fairly loosely in the cell. The partial occupancy of O(1) may be one reason for the unusual behavior of the O(2) atom.

The ammonium and potassium salts, as previously stated,[8] are isostructural. The choices of origin in the two structures differ by 0, 0, $^1/_2$ as indicated in the fractional coordinates.

The difference in residuals between the correct and incorrect absolute configurations was expected to be noticeable for a structure of this accuracy and with so many anomalous scatterers. Structure factors with and without the $\Delta f' + i\Delta f''$ terms were calculated and compared against F_o using the final atomic parameters listed in this paper. The difference in residuals for these two calculations was 2.5%, indicating significant anomalous scattering. However, as stated in the Experimental Section, both space groups refined to the same R values. The main point is that the metal–metal distance is correct to within the stated error.

Table V

Atoms	Contact dist, Å	Symmetry position
K(1)-Cl(1)	3.419 (5)	$x, y, z + 1$
K(1)-Cl(2)	3.274 (5)	$x, y, z + 1$
K(1)-Cl(3)	3.196 (4)	$-x, y - x, -^1/_3 - z$
K(1)-Cl(4)	3.333 (5)	$-x, y - x, -^1/_3 - z$
K(2)-Cl(2)	3.302 (9)	$x, y, z + 1$
K(2)-Cl(3)	3.310 (9)	$-x, y - x, -^1/_3 - z$
K(1)-Cl(1)	3.407 (5)	$-x, y - x, -^1/_3 - z$
K(1)-Cl(2)	3.210 (5)	$-x, y - x, -1 - z$
K(1)-Cl(2)	3.380 (5)	$x - y, -1 - y, -^2/_3 - z$
K(1)-Cl(3)	3.405 (5)	$y + 1, x, -z$
K(1)-Cl(3)	3.326 (4)	$x - y, -1 - y, ^1/_3 - z$
K(1)-Cl(4)	3.704 (6)	$y + 1, x, -z$
K(2)-Cl(1)	3.161 (6)	$y + 1, x, -1 - z$

The exact water content of these salts seems variable and is not entirely certain. Analytical data have tended to indicate the presence of two water molecules per formula unit, which means six per unit cell. On the other hand, full occupancy of both the O(1) sixfold position and the O(2) threefold position would make a total of nine in the unit cell and correspond to the formula $M_3Tc_2Cl_8 \cdot 3H_2O$. In the case of the ammonium salt we were unable to specify the degree of occupancy of the oxygen positions, but it did seem clear, and we so stated, that at least the O(1) position was not fully occupied. Koz'min and Novitskaya do not even report positions for the oxygen atoms. Curiously, the measured density they reported corresponds more closely to the trihydrate than to the dihydrate, a fact which they fail to comment on. We were unable to make reliable density measurements but found that O(1) refines best with an occupancy factor of 0.79. The behavior of O(2), as already noted, is inconsistent, and we did not attempt to refine an occupancy factor for it. If that position is fully occupied, our crystal would have been represented by the formula $K_3Tc_2Cl_8 \cdot 2.58H_2O$.

Comparison with Previous Work. The structure of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ was arbitrarily refined in space group $P3_221$, since the enantiomorphous space groups were indistinguishable with the available film data. We have refined here the structure of the potassium compound in the space group $P3_221$ this again being an arbitrary choice since the two enantiomorphs refined equally well. The coordinates in the present case are related to those given previously by a coordinate shift of 0, 0, $^1/_2$ but are considerably more accurate.

It is interesting to note that the choice made in the case of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ for the positions of nitrogen atoms, which in that case were not objectively distinguishable from water molecules, has been proven to be correct. When the appropriate transformation of coordinates is made, the positions assigned to N(1) and N(2) are very similar to those found for K(1) and K(2).

Acknowledgment. We are grateful to the National Science Foundation for support under Grant No. 33142X. We wish to thank Dr. Douglas Collins for many helpful discussions.

Registry No. $K_3Tc_2Cl_8 \cdot nH_2O$, 55569-91-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50005Z-9-75.

References and Notes

(1) (a) F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, **145**,

1305 (1964); (b) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965); (c) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965); (d) F. A. Cotton, *ibid.*, **4**, 334 (1965).
(2) (a) F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965); (b) W. K. Bratton and F. A. Cotton, *Inorg. Chem.*, **9**, 789 (1970).
(3) J. D. Eakins, G. D. Humphreys, and C. F. Mellish, *J. Chem. Soc.*, 6012 (1963).
(4) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 924 (1967).
(5) (a) J. G. Norman and H. J. Kolari, *J. Chem. Soc., Chem. Commun.*, 303 (1974); (b) *J. Am. Chem. Soc.*, **97**, 33 (1975); (c) M. B. Cingi and E. Tondello, *Inorg. Chim. Acta*, **11**, L3 (1974).
(6) (a) F. A. Cotton and E. Pedersen, *Inorg. Chem.*, **14**, 383 (1975); (b) *J. Am. Chem. Soc.*, **97**, 303 (1975).
(7) M. I. Glinka, A. F. Kuzina, and V. I. Spitsyn, *Zh. Neorg. Khim.*, **18**, 403 (1973).
(8) P. A. Koz'min and G. N. Novitskaya, *Zh. Neorg. Khim.*, **17**, 3138 (1972).
(9) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).
(10) Calculations were performed on an IBM 360 computer using the following programs: DATARED by Frenz for data reduction; FOURIER by Robinson and Dellaca and based on Zalkin's FORDAP; NUCLS, a full-matrix least-squares program by Ibers and Doedens based on Busing and Levy's ORFLS program; a modified version of SADIAN by Bauer for calculating atomic distances and angles; PERFACT by Frenz for analyzing structure factors and weighting schemes; ORTEP by Johnson for illustrations; the function and error program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen; LIST by Snyder for listing data.
(11) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", Macmillan, London, 1968, pp 425–426.
(12) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, in press.
(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(14) Supplementary material.
(15) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).
(16) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65201

Characterization and Structures of Two Protonated Tetracyanomolybdenum(IV) Oxy Ions

P. R. ROBINSON,[1] E. O. SCHLEMPER,* and R. KENT MURMANN*

Received January 27, 1975 AIC50064C

The structures of the two blue complex ions $[MoO(H_2O)(CN)_4]^{2-}$ and $[MoO(OH)(CN)_4]^{3-}$ have been determined using scintillation counter techniques in three-dimensional X-ray diffraction studies. $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/m$ with unit cell dimensions $a = 14.873$ (3) Å, $b = 12.128$ (5) Å, $c = 8.921$ (3) Å, and $\beta = 146.60$ (2)°; $\rho_{obsd} = 2.21$ (6) g/cm^3, $\rho_{calcd} = 2.200$ (3) g/cm^3, and $Z = 2$. $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ crystallizes in the monoclinic space group $I2/c$ with unit cell dimensions $a = 12.445$ (2) Å, $b = 10.664$ (3) Å, $c = 18.111$ (3) Å, and $\beta = 125.60$ (2)°; $\rho_{obsd} = 1.61$ (3) g/cm^3, $\rho_{calcd} = 1.642$ (2) g/cm^3, and $Z = 4$. The structures were resolved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. The final conventional R factor, based on 1965 independent reflections whose intensities were above 3σ, was 2.3% for $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$, and that based on 1043 independent reflections was 3.4% for $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$. In both negative ions the ligands are in distorted octahedral positions about the molybdenum atoms with trans oxygen atoms, and the molybdenum atoms are not coplanar with the cyanide ions. Mo–O bond distances of 2.271 (4) and 1.668 (5) Å for $[MoO(H_2O)(CN)_4]^{2-}$ suggest that this ion is the oxoaquo complex rather than the previously suggested dihydroxo complex. Mo–O bond distances of 2.007 (7) and 1.698 (7) Å were found for $[MoO(OH)(CN)_4]^{3-}$, and the molybdenum is disordered with respect to the center of symmetry. Spectrophotometric titrations, ir spectra, and Tyndall tests were used to show that *blue* $[Mo(O)(OH)(CN)_4]^{3-}$ is the primary aqueous species present from pH 10 to pH 13, that $[MoO(H_2O)(CN)_4]^{2-}$ is the blue complex ion near neutral pH's, and that the green solutions which were reported as $[Mo(OH)_2(CN)_4]^{2-}$ are a mixture of $[MoO(H_2O)(CN)_4]^{2-}$ and colloidal molybdenum(IV) hydroxide.

Introduction

In a continuing study of the aqueous chemistry and the exchange kinetics of oxy ions of the second- and third-row transition groups, we carried out some solution equilibrium experiments on the previously known $K_4[MoO_2(CN)_4]$. Our interests were primarily in the equilibrium constants for acid–base equilibria occurring in aqueous media. These were to be used in interpreting the kinetic experiments on ^{18}O exchange with solvent water.[2] However, discrepancies with the literature became apparent in the acid–base behavior which necessitated a complete study of the nature of the ions involved. The structure of the solid *red* salt $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ has been reported.[3] The complex ion has a distorted octahedral structure with trans oxygen atoms. Addition of water gives a *blue* solution which has commonly been formulated as $[MoO(OH)(CN)_4]^{3-}$. Previous workers[4,5] have said that addition of dilute acid converts this substance to *green* $[Mo(OH)_2(CN)_4]^{2-}$. Other workers[6,7] have reported the initial blue ion to be $[Mo(OH)_3(H_2O)(CN)_4]^{3-}$ and the ion formed in neutral–acidic media to be blue. Our spectrophotometric studies indicated that two blue species existed in the pH range 12–7 with slight spectral differences and that in slightly acidic media (pH 5) kinetically unstable green solutions were obtained. The purpose of this study was to determine the structures of the two blue ions and the equilibrium constant relating them.

Experimental Section

A. Preparation of the Compounds. All reagents used were analytical grade. pH titrations were accomplished potentiometrically using a Leeds & Northrup "Zeromatic" potentiometer, and redox titrations were done potentiometrically using a Pt-wire measuring electrode vs. SCE. Spectrophotometric studies were carried out on a temperature-controlled Beckman DU spectrophotometer.

$K_4[MoO_2(CN)_4]$ was prepared using the method of Jakob and Turkiewicz[8] with the following modifications. Since the solid compound reacted with atmospheric CO_2, all crystallization, collection, and purification steps were performed under purified $N_2(g)$. Instead of solid KOH, saturated solutions of KOH at 0° were used to precipitate the salt. A small excess of KCN was added to the complex solution before precipitation to prevent dissociation of the complex ion. Titrations at 0° of the vacuum-dried salt with 1 N HCl to a pH of 7.2 yielded an equivalent weight of 195 ± 4 which agrees with that of 194.2 calculated for $K_4[MoO_2(CN)_4]$. Although precautions were taken to ensure that the compound remained dry during mailing for analysis, the extremely hygroscopic salt apparently picked up some water during transfer. Anal. Calcd for $K_4MoO_2C_4N_4\cdot{}^1/_4H_2O$: C, 12.22; N, 14.25; H, 0.13. Found: C, 12.16; N, 13.86; H, 0.09. (These and all other C, N, and H analyses were made by Galbraith Laboratories, Knoxville, Tenn.)

$K_3[MoO(OH)(CN)_4]$ was prepared from $K_4[MoO_2(CN)_4]$ by the