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

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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

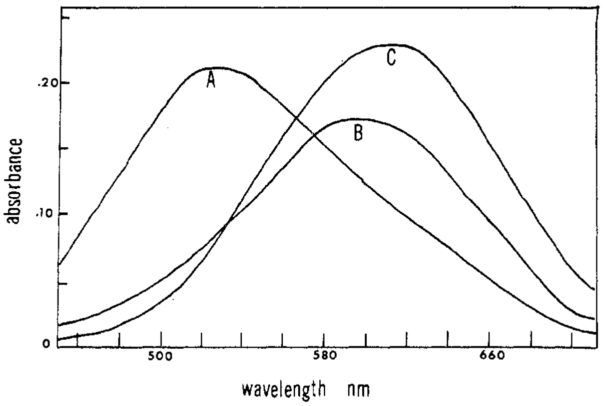

Figure 1. Visible absorption spectra: (A) $[MoO_2(CN)_4]^{4-}$, 7.8 × 10^{-3} *M*; (B) $[MoO(OH)(CN)_4]^{3-}$, 4.06 × 10^{-3} *M*; (C) $[MoO(OH_2)(CN)_4]^{2-}$, 5.4 × 10^{-3} *M*.

addition of methanol under $N_2(g)$ to aqueous solutions of the dioxo salt at 0°, i.e.

$$H_2O + K_4Mo(O)_2(CN)_4 \rightarrow K_3MoO(OH)(CN)_4(s) + K^+ + OH^-$$

The blue solid was washed with ethanol and ether and dried under vacuum at 110°. Titrations with 1 *M* HCl yielded an equivalent weight of 355 ± 7, which agrees with that of 350.3 calculated for $K_3[MoO(OH)(CN)_4]$. Titrations with $K_3[Fe(CN)_6]$ according to the method of van de Poel and Neumann[4] to oxidize the Mo(IV) to Mo(VI) yielded a molecular weight of 352 ± 3. Anal. Calcd for $K_3MoO_2N_4C_4H$: C, 13.71; N, 15.99; H, 0.29. Found: C, 13.61; N, 16.19; H, 0.31.

$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ was prepared by mixing solutions of $K_3[MoO(OH)(CN)_4]$ and $[Cr(en)_3]Cl_3$ in 0.1 *N* KOH at 0°. The crystals were collected on a filter, washed with water, and dried at room temperature. Anal. Calcd for $MoCrO_3C_{10}N_{10}H_{27}$: C, 24.85; N, 28.98; H, 5.63. Found: C, 24.79; N, 28.94; H, 5.77.

B. Characterization Studies. Spectrophotometric studies showed the red $[MoO_2(CN)_4]^{4-}$ ion to have an absorption maximum at 520 nm, ϵ 27.7 (8), the blue $[MoO(OH)(CN)_4]^{3-}$ ion to have a maximum at 595 nm, ϵ 41.9 (1), and the blue $[MoO(H_2O)(CN)_4]^{2-}$ ion a maximum at 610 nm, ϵ 42.5 (4). The visible spectra of these three ions are shown in Figure 1. Titrations of $K_4Mo(O)_2(CN)_4$ with HCl showed one end point at 2.0 ± 0.1 equiv of acid/mol of complex at pH ~7.2. Using pH and visible spectra the two acid dissociation constants were determined at μ = 1.00 (KNO_3) (25°): $K_1 = (1.2 \pm 0.1) \times 10^{-11}$; $K_2 = (6.3 \pm 0.8) \times 10^{-13}$. Addition of acid to neutral blue solutions to bring them to a slightly acidic media (pH 5–6) yielded blue solutions which turned green after a few minutes. The pH of these green solutions increased slowly with time, indicating hydrolysis of CN^- from the complex to form HCN. The absorbance of these solutions (pH 5–6) behaved erratically with time. Addition of base to the green solutions to pH 7 resulted in blue solutions whose absorption maximum was 595 nm and whose absorbance was less than what it had been before the addition of the acid. A tan solid settled out by centrifugation of these solutions. Tyndall tests on the green solutions indicated the presence of a suspended tan solid. The ir spectrum of this tan solid showed no peaks in the 1800–2500-nm range, which indicated that it contained no cyanide ion. From the above observations, it was concluded that the green solution was a mixture of the blue $[MoO(H_2O)(CN)_4]^{2-}$ and a colloidal tan solid, polymeric molybdenum hydroxide.

Both $K_4MoO_2(CN)_4$ and $K_3MoO(OH)(CN)_4$ react rapidly with atmospheric CO_2 to produce mixtures of carbonate salts which may account for some of the observations of an earlier study. No evidence could be found for reaction with atmospheric oxygen under dry, CO_2-free conditions. The asymmetric O–Mo–O stretch in $MoO_2(CN)_4^{4-}$ occurs at 850 cm^{-1} while the Mo–O stretch (multiply bonded) occurs at 900 cm^{-1} in $Mo(O)(OH)(CN)_4^{3-}$. These are consistent with the bond lengths determined in the X-ray structures.

C. Single-Crystal X-Ray Structures Studies. Preliminary film X-ray studies of $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ indicated that the crystals were monoclinic. The systematic extinctions of odd *k* on 0*k*0 indicated the space group $P2_1$ or $P2_1/m$. The film studies of $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ revealed a monoclinic cell in space group *Ic* or *I*2/*c* based on the absence of odd values of $h + k + l$ for *hkl* and odd *l* for *h*0*l*. X-Ray intensity measurements were made using the θ–2θ scan technique on suitable single crystals which were centered on a Picker four-circle diffractometer. Cell constants and the setting angles for all measured intensities were determined by least-squares refinement of 25–35 centered intense high-angle reflections. These were obtained using Mo $K\alpha_1$ radiation (λ 0.70926 Å) with a small takeoff angle and with a narrow vertical slit at the counter. For intensity measurements the diffracted Mo $K\alpha$ radiation was filtered through 1 mil of niobium foil in front of a 3 mm × 3 mm receiving aperture at a takeoff angle of 2.0°. The counting rate never exceeded 8000 counts/sec and was therefore in the linear region of the counter.

Standard reflections were measured at regular intervals so that corrections could be made for possible changes in intensity due to decomposition of the crystals or instrument variation. The data sets were corrected for background, Lorentz, and polarization effects using local computing programs and facilities[9] and formulas described by Corfield, Doedens, and Ibers.[10] The scattering factor tables used for molybdenum, platinum, and chromium were those of Cromer and Waber,[11] while the anomalous scattering effects for those atoms were taken from Cromer.[12] Scattering factor tables for oxygen, nitrogen, and carbon atoms were taken from Ibers,[13] and those for hydrogen atoms were from Stewart, Davidson, and Simpson.[14] Anomalous scattering effects for the heavy metals were included in F_c for the refinements.

$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$. Intensity measurements were made on a crystal of dimensions 0.092 × 0.093 × 0.226 mm. A relatively small crystal was chosen because of the high linear absorption coefficient μ = 86 cm^{-1} for Mo $K\alpha$ radiation. The crystal was mounted with the c^* axis of the crystal coincident with the ϕ axis of the diffractometer. The setting angles of 35 reflections were used to refine the cell constants, which were a = 14.873 (3) Å, b = 12.128 (5) Å, c = 8.9251 (3) Å, and β = 146.60 (2)°. The density calculated on the basis of two formula units per unit cell was 2.200 (3) g/cm^3, which agrees with the observed density of 2.21 (6) g/cm^3 obtained by flotation in a CCl_4–CBr_4 solution. A total of 4799 reflections were measured to a 2θ angle of 55°, using a scan rate of 1°/min for the variable nonsymmetric 2θ scan, which was taken from 0.35° below the 2θ setting angle for Mo $K\alpha_1$ to 0.40° above the 2θ setting angle for Mo $K\alpha_2$. Stationary-background counts of 20 sec were taken at both the high- and low-angle ends of the scan. Four reflections covering a range of 90° in both χ and ϕ chosen as standards were measured every 50 reflections. Twenty fairly intense reflections were measured every 500 reflections and these two sets of standards were used for a decomposition correction. A plot of intensity vs. reflection number indicated a decrease in intensity of about 10% over the 10-day data collection period. The decrease was essentially linear in two segments, the separation of which corresponded to an interruption in the data collection for instrument repairs.

The dimensions of the crystal and the indices of the bonding faces were measured for absorption correction. From the 4799 measured intensities 2137 independent data points were obtained by averaging. A total of 1965 of these had F_o^2 greater than $3\sigma(F_o^2)$, where $\sigma = (\sigma^2_{counting} + (0.03F_o^2)^2)^{1/2}$, and these were used to determine and refine the structure.

From a three-dimensional Patterson synthesis the positions of the platinum and molybdenum atoms were located, and these positions were used to phase the F_o values for a subsequent Fourier synthesis. Since no significant difference in the intensities of selected Friedel pairs was observed, the space group $P2_1/m$ was assumed. This choice was subsequently verified by the refinement. The platinum and molybdenum atoms were found to lie on the mirror plane at $y = {}^1/_2$. The *x* and *y* coordinates of these atoms were refined by full-matrix least squares minimizing the function $\sum w(|F_o^2| - |kF_c|^2)^2$ where the weight is $w = 1/\sigma^2(F_o^2)$. A three-dimensional Fourier synthesis was used to locate all other nonhydrogen atoms. The ligand oxygen atoms were also found to lie on the mirror plane. Least-squares refinement of the positions of all nonhydrogen atoms with isotropic thermal factors converged with $R = \sum|F_o^2 - kF_c^2|/\sum F_o^2 = 0.081$ and $r = (\sum w(F_o^2 - kF_c^2)^2/\sum F_o^4)^{1/2} = 0.139$. Several more cycles with anisotropic thermal parameters for all nonhydrogen atoms and with an isotropic extinction parameter[15] gave agreement factors R = 0.039 and r = 0.070.

A difference Fourier synthesis based on this refinement was used

Table II.[a] Final Atomic Parameters for $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.21076 (2)	$^1/_4$	0.00473 (4)	0.01049 (4)	0.00562 (2)	0.0310 (1)	0	0.01553 (6)	0
Mo	−0.32223 (6)	$^1/_4$	−0.1141 (1)	0.01048 (7)	0.00477 (3)	0.0341 (2)	0	0.0161 (1)	0
O(1)	−0.2902 (5)	$^1/_4$	0.1832 (9)	0.0188 (8)	0.0577 (3)	0.053 (2)	0	0.029 (1)	0
O(2)	−0.3506 (6)	$^1/_4$	−0.3387 (9)	0.0181 (8)	0.009 (4)	0.045 (2)	0	0.0248 (1)	0
O(3)	−0.2291 (5)	0.0707 (4)	0.432 (1)	0.02932 (9)	0.0096 (3)	0.116 (3)	0.0076 (4)	0.054 (2)	0.0173 (8)
N(1)	−0.0257 (5)	0.0668 (4)	0.3107 (9)	0.0191 (7)	0.0080 (3)	0.067 (2)	0.0036 (4)	0.032 (1)	0.0064 (7)
N(2)	−0.5757 (5)	0.0492 (3)	−0.3705 (9)	0.0174 (7)	0.0074 (3)	0.058 (2)	−0.0021 (4)	0.026 (1)	−0.0012 (7)
N(3)	0.1267 (5)	0.1393 (4)	0.0394 (9)	0.0175 (7)	0.0116 (4)	0.053 (2)	−0.0009 (4)	0.027 (1)	0.0035 (8)
N(4)	0.2910 (5)	0.1383 (3)	−0.0377 (8)	0.0182 (7)	0.0056 (3)	0.062 (2)	0.0009 (3)	0.029 (1)	0.0000 (6)
C(1)	−0.1306 (5)	0.1288 (4)	0.1644 (9)	0.0131 (7)	0.0062 (3)	0.043 (2)	0.0003 (4)	0.021 (1)	0.0001 (7)
C(2)	−0.4918 (5)	0.1207 (4)	−0.2870 (9)	0.0125 (6)	0.0061 (3)	0.041 (2)	−0.0001 (4)	0.019 (1)	−0.0006 (7)
C(3)	0.093 (2)	0.211 (1)	0.139 (3)	0.022 (2)	0.021 (3)	0.077 (7)	0.007 (2)	0.037 (4)	0.018 (4)
C(4)	0.008 (2)	0.182 (1)	−0.026 (3)	0.019 (2)	0.016 (1)	0.058 (6)	−0.004 (1)	0.030 (3)	−0.003 (3)
C(5)	0.406 (2)	0.192 (1)	0.018 (3)	0.017 (2)	0.0083 (8)	0.054 (6)	0.004 (1)	0.027 (3)	0.006 (2)
C(6)	0.329 (2)	0.201 (1)	−0.129 (3)	0.022 (3)	0.0081 (8)	0.067 (7)	0.001 (1)	0.036 (4)	0.000 (2)

[a] Numbers in parentheses in this and subsequent tables are the standard deviations from the least-squares refinement.

to locate the hydrogen atoms bonded to oxygens, while the remaining hydrogen atoms were found using a combination of the difference Fourier and calculated chemically reasonable positions consistent with the space group $P2_1/m$. The positions of these hydrogen atoms are given in Table I.[16] With positional and thermal parameters for the hydrogen atoms fixed, two additional least-squares cycles yielded $R = 0.033$ and $r = 0.060$. The conventional agreement factor $\sum(||F_o| - |kF_c||)/\sum F_o$ was 0.023. The observed and calculated structure factors (×10) are available,[16] and the final atomic positional and thermal parameters are presented in Table II.

$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$. Efforts to crystallize $[MoO(OH)(CN)_4]^{3-}$ as the sodium, potassium, and $[Co(en)_3]^{3+}$ salts yielded unsatisfactory results,[17] after which suitable single crystals of $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ were obtained using the method described. The crystal used for the intensity measurements was defined by ten faces, and the mean diameter of the approximately spherical crystal was 0.135 mm. The linear absorption coefficient ($\mu = 12.27$) for Mo Kα radiation suggests that a larger crystal might have been used, but larger crystals were not obtained. The crystal was centered on the diffractometer with the $10\bar{1}$ axis of the crystal coincident with the ϕ axis of the diffractometer. The setting angles of 26 reflections were used to determine the cell constants $a = 12.445$ (2) Å, $b = 10.664$ (3) Å, $c = 18.111$ (3) Å, and $\beta = 125.60$ (2)°. The density calculated for four formula units per unit cell was 1.642 (2) g/cm^3, to be compared with the observed density of 1.61 (3) g/cm^3 obtained by flotation in a CCl_4–CBr_4 solution. A total of 4012 reflections were measured out to a 2θ angle of 45°. A scan rate of 1°/min was used for all but 826 of the reflections, and background counts of 20 sec were taken at the high- and low-angle ends of the scan, which ranged from 0.45° below the 2θ setting angle for Mo Kα_1 to 0.70° above the 2θ setting angle for Mo Kα_2. In order to improve the reliability of the lower intensity measurements, all reflections whose intensities were less than 150 counts/min but still above background were remeasured using a scan rate of 0.25°/min with stationary-background counts of 100 sec. Three reflections covering a wide range in both χ and ϕ were measured every 50 reflections, and 16 fairly intense reflections were measured every 500 reflections so that corrections for decomposition of the crystal or for instrument drift could be made. The data from $2\theta = 0$ to 20° included all equivalent forms, while the remainder of the data included all but those reflections whose h indices were negative. A plot of the standard reflections indicated an overall decrease in intensity of about 4%, and a correction was made for this decrease.

The dimensions and morphology of the crystal were determined optically so that corrections for absorption could be made. From the 4443 measured intensities, 1243 independent data points were obtained by averaging. A total of 1043 of these had intensities greater than 3σ and were used to determine and refine the structure. From a three-dimensional Patterson synthesis the positions of the molybdenum and chromium atoms were located and used to phase the F_o values for a subsequent Fourier synthesis. The differences in intensities of Friedel's pairs was slight, but there was enough variance to cause us to reserve judgment on whether the space group was centric. For convenience, the space group $I2/c$ was assumed, and this choice was eventually verified by the refinement. The molybdenum atom was assumed to lie on the center of symmetry, and the chromium atom was found to lie on the twofold axis. Isotropic temperature factors and variable positional parameters for these atoms were refined by full-matrix three-dimensional least-squares analysis, and a three-dimensional Fourier synthesis based on phases from this refinement was used to locate all other nonhydrogen atoms. Refinement of the positions of all nonhydrogen atoms with isotropic temperature factors converged with $R = 0.175$ and $r = 0.386$. Several cycles with anisotropic thermal factors yielded $R = 0.073$ and $r = 0.162$. A combination of a difference Fourier synthesis based on this refinement and calculated chemically reasonable positions consistent with the space group $I2/c$ was used to locate all ethylenediamine hydrogen atoms. The positions of these atoms are presented in Table III.[16] With the positional parameters and isotropic thermal parameters for the hydrogen atoms fixed, two additional least-squares cycles yielded $R = 0.054$ and $r = 0.108$. A difference Fourier synthesis based on this refinement indicated some residual electron density which was difficult to account for. For this reason a refinement in the space group Ic was made, and agreement factors $R = 0.051$ and $r = 0.095$ were obtained. This refinement was based upon 225 variables, and, according to the statistical test of Hamilton,[18] it could not be preferred over the centric refinement, which was based upon 121 variables.

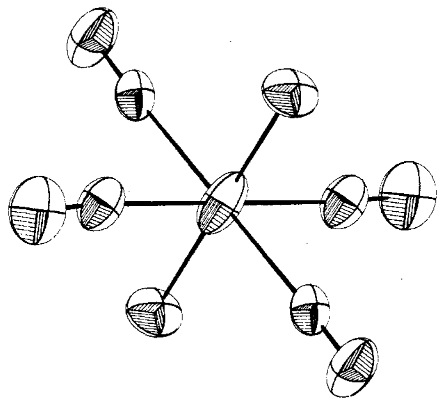

Figure 2. Structure of $[MoO(OH)(CN)_4]^{3-}$ based on refinement with the Mo on the center of symmetry.

It was observed at this time that the molybdenum atom had a large thermal vibration along the axis formed by the two ligand oxygens (Figure 2). This, together with the fact that the ligand oxygens were not expected to be equivalent, led us to remove the requirement that the molybdenum atom lie on the center of symmetry. Refinement with two half molybdenum atoms yielded agreement factors $R = 0.050$ and $r = 0.103$. Since a total of 124 variables was used for this refinement, the statistical test of Hamilton[18] showed that this model was preferable to either the previous centric or acentric refinement at the 99.5% confidence level. The existence of two different molybdenum positions indicated that there might also be two different positions for the cyanide nitrogens. A refinement based on nitrogens placed so as to make the Mo–C–N angle 180° gave agreement factors $R = 0.051$ and $r = 0.104$ based on 126 variables, which showed that this model could not be favored over the previous one. The observed and calculated structure factors (×10) for the model without disordered nitrogens are available,[16] while final positional and thermal parameters are found in Table IV.

Table IV. Final Atomic Parameters for $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.4923 (8)	0.0152 (5)	0.4906 (5)	0.0060 (3)	0.0042 (4)	0.0027 (2)	−0.0008 (3)	0.0022 (2)	−0.0007 (2)
Cr	0.0	−0.02153 (9)	0.25	0.0048 (1)	0.0048 (1)	0.00202 (6)	0.0	0.00156 (7)	0.0
O(1)	0.3610 (3)	0.0869 (3)	0.3977 (2)	0.0064 (4)	0.0082 (4)	0.0032 (2)	0.0004 (3)	0.0011 (2)	0.0002 (2)
O(2)	0.451 (1)	0.1455 (7)	0.2503 (8)	0.024 (2)	0.0083 (8)	0.0050 (4)	−0.0018 (9)	0.005 (1)	−0.0006 (6)
N(1)	0.3065 (5)	−0.0720 (5)	0.5634 (4)	0.0126 (7)	0.0141 (7)	0.0056 (3)	−0.0011 (5)	0.0055 (4)	−0.0009 (3)
N(2)	0.3986 (5)	−0.2652 (4)	0.3844 (3)	0.0138 (7)	0.0079 (5)	0.0056 (3)	−0.0030 (5)	0.0065 (4)	−0.0029 (3)
N(3)	0.0989 (4)	−0.1683 (4)	0.3413 (3)	0.0076 (5)	0.0062 (4)	0.0030 (2)	0.0009 (3)	0.0023 (3)	0.0004 (2)
N(4)	0.0930 (4)	0.1100 (4)	0.3524 (3)	0.0075 (5)	0.0067 (4)	0.0038 (2)	−0.0002 (4)	0.0031 (3)	−0.0009 (3)
N(5)	0.1443 (4)	0.0103 (3)	−0.2738 (3)	0.0073 (5)	0.0070 (4)	0.0036 (3)	0.0005 (3)	0.0032 (3)	0.0005 (2)
C(1)	0.3715 (5)	−0.0430 (5)	0.5409 (4)	0.0073 ( )	0.0076 (5)	0.0033 (3)	−0.0013 (5)	0.0025 (4)	−0.0019 (3)
C(2)	0.4338 (5)	−0.1732 (5)	0.4225 (3)	0.0067 (6)	0.0081 (6)	0.0029 (3)	0.0006 (4)	0.0029 (3)	−0.0005 (3)
C(3)	0.0704 (5)	−0.2870 (4)	0.2894 (3)	0.0116 (7)	0.0056 (5)	0.0038 (3)	0.0022 (4)	0.0041 (4)	0.0004 (3)
C(4)	−0.0334 (6)	0.1078 (5)	0.0954 (4)	0.0102 (7)	0.0121 (7)	0.0036 (3)	0.0003 (5)	0.0038 (4)	0.0017 (4)
C(5)	0.1137 (6)	0.0973 (5)	0.1631 (4)	0.0127 (8)	0.0094 (6)	0.0056 (4)	−0.0012 (5)	0.0062 (5)	0.0007 (4)

Table V. Bond Distances and Angles in $[Pt(en)_2]^{2+}$

Dist	Value, Å	Angle	Value, deg
Pt-N(4)	2.036 (4)	N(3)-Pt-N(4)	178.8 (3)
Pt-N(3)	2.024 (4)	N(4)-C(5)-C(6)	105 (1)
N(3)-C(3)	1.59 (2)	N(4)-C(6)-C(5)	108 (1)
N(3)-C(4)	1.42 (1)	N(3)-C(3)-C(4)	108.6 (9)
N(4)-C(5)	1.47 (1)	N(3)-C(4)-C(3)	100.0 (8)
N(4)-C(6)	1.53 (1)	N(3)-Pt-N(3)	83.1 (3)
C(3)-C(4)	1.53 (2)	N(4)-Pt-N(4)	83.4 (2)
C(5)-C(6)	1.48 (1)	N(3)-Pt-N(4)	96.8 (2)

Table VI. Bond Distances and Angles in $[Cr(en)_3]^{3+}$

Dist	Value, Å	Angle	Value, deg
Cr-N(3)	2.061 (5)	Cr-N(3)-C(3)	109.0 (3)
Cr-N(4)	2.080 (4)	Cr-N(4)-C(4)	109.4 (3)
Cr-N(5)	2.079 (5)	Cr-N(5)-C(5)	109.5 (3)
C(3)-N(3)	1.491 (6)	N(3)-Cr-N(4)	92.0 (2)
C(4)-N(4)	1.500 (7)	N(3)-Cr-N(5)	91.4 (2)
C(5)-N(5)	1.504 (7)	N(4)-Cr-N(5)	92.7 (2)
C(3)-C(3)[a]	1.48 (1)	N(3)-C(3)-C(3)[a]	108.7 (3)
C(4)-C(5)	1.505 (8)	N(4)-C(4)-C(5)	107.5 (4)

[a] Related by center of symmetry, or twofold axis.

Table VII. Bond Distances and Angles in $[MoO(H_2O)(CN)_4]^{2-}$

Dist	Value, Å	Angle	Value, deg
Mo-O(1)	2.271 (4)	O(1)-Mo-O(2)	179.0 (3)
Mo-O(2)	1.668 (5)	O(1)-Mo-C(1)	81.8 (2)
Mo-C(1)	2.150 (8)	O(1)-Mo-C(2)	79.9 (3)
Mo-C(2)	2.166 (6)	Mo-C(2)-N(2)	178.0 (4)
C(1)-N(1)	1.141 (7)	Mo-C(1)-N(1)	177.8 (3)
C(2)-N(2)	1.143 (6)		

Results

Bond distances and angles for $[Pt(en)_2]^{2+}$, $[Cr(en)_3]^{3+}$, $[MoO(H_2O)(CN)_4]^{2-}$, and $[MoO(OH)(CN)_4]^{3-}$ are shown in Tables V–VIII and in Figures 3–6. $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ consists of discrete square-planar $[Pt(en)_2]^{2+}$ ions and distorted octahedral $[MoO(H_2O)(CN)_4]^{2-}$ ions. The latter has a nearly linear trans arrangement of the coordinated oxygens (the angle O(1)–Mo–O(2) is 179.0 (3)°). The possibility of either C or N bonding of the cyano ligands was checked by refinement of the isocyanide structure.

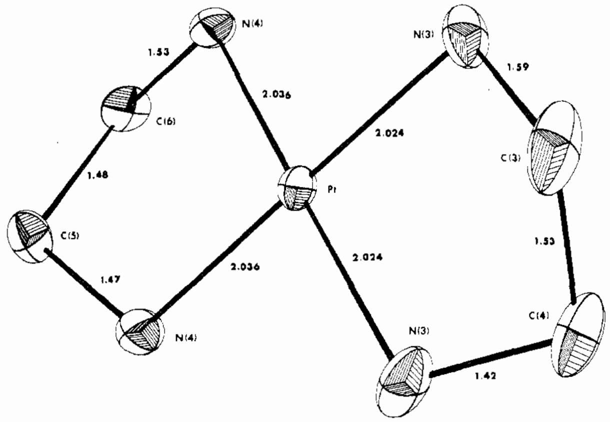

Figure 3. Bond distances in $[Pt(en)_2]^{2+}$.

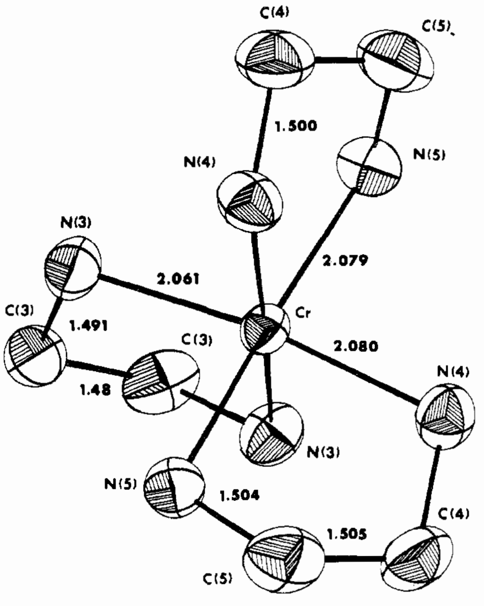

Figure 4. Bond distances in $[Cr(en)_3]^{3+}$.

Table VIII. Bond Distances and Angles in $[MoO(OH)(CN)_4]^{3-}$

Dist	Value, Å	Angle	Value, deg	Angle	Value, deg
Mo-Mo[a]	0.428 (8)	Mo-C(1)-N(1)	177.6 (6)	C(1)-Mo-C(2)[b]	91.2 (3)
Mo-O(1)	1.698 (7)	Mo-C(2)-N(2)	176.4 (5)	C(1)-Mo[b]-C(2)[b]	91.8 (4)
Mo[b]-O(1)	2.077 (7)	Mo[b]-C(1)-N(1)	171.1 (5)	C(1)-Mo-O(1)	92.4 (4)
Mo-C(1)	2.25 (1)	Mo[b]-C(2)-N(2)	172.3 (5)	C(1)-Mo[b]-O(1)	87.0 (3)
Mo[b]-C(1)	2.10 (1)	O(1)-Mo-O(1)[b]	174.0 (4)	C(1)-Mo-O(1)[b]	97.5 (3)
Mo-C(2)	2.246 (9)	C(1)-Mo-C(1)[b]	169.5 (2)	C(2)-Mo-O(1)	92.4 (4)
Mo[b]-C(2)	2.117 (9)	C(2)-Mo-C(2)[b]	169.3 (2)	C(2)-Mo[b]-O(1)	86.4 (3)
C(1)-N(1)	1.139 (7)	C(1)-Mo-C(2)	84.0 (3)	C(2)[b]-Mo-O(1)	97.4 (3)
C(2)-N(2)	1.130 (6)	C(1)-Mo[b]-C(2)	91.1 (3)	C(2)[b]-Mo[b]-O(1)	83.5 (3)

[a] Distance between disordered Mo positions. [b] This refers to an atom with positions related by symmetry to those given in Table IV.

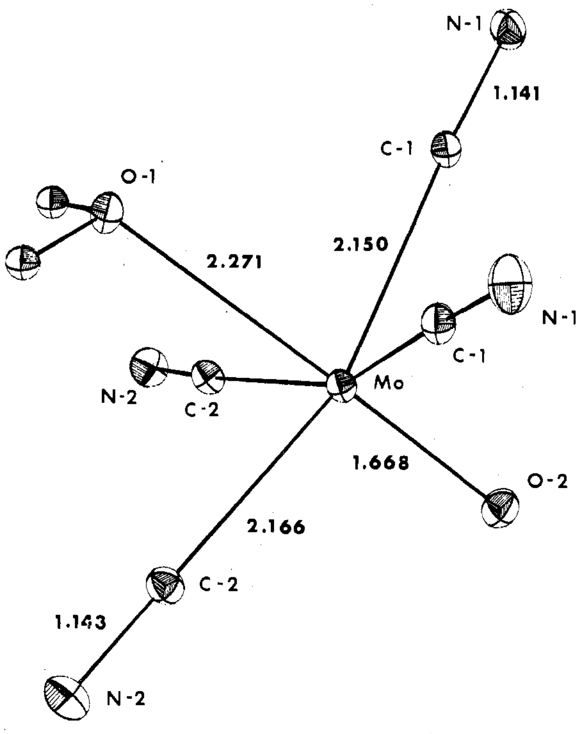

Figure 5. Bond distances in $[MoO(H_2O)(CN)_4]^{2-}$.

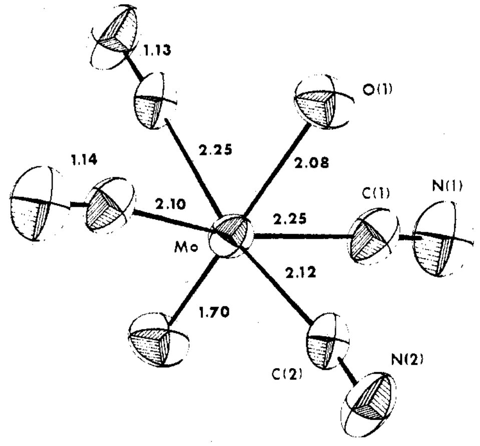

Figure 6. Bond distances in $[MoO(OH)(CN)_4]^{3-}$.

Table IX. Selected Interionic Distances (Hydrogen Bonds) for $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$

Atoms	Dist, Å	Atoms	Dist, Å
O(3)- - -O(1)	2.667 (5)	N(1)- - -N(4)	3.407 (8)
O(3)- - -N(1)	2.802 (6)	N(1)- - -N(3)	3.230 (8)
O(3)- - -N(2)	2.860 (6)	N(2)- - -N(4)	3.26 (1)
O(3)- - -N(3)	3.18 (2)	N(2)- - -N(3)	3.10 (2)

Agreement factors for this structure were $R = 0.038$ and $r = 0.072$ compared with $R = 0.33$ and $r = 0.060$ for the C-bonded arrangement, indicating that the carbon-bonded arrangement is more consistent.

The ethylenediamine carbons in the $[Pt(en)_2]^{2+}$ ion are disordered, with the alternating pairs related by mirror symmetry. These ions are associated by hydrogen bonding to the negative ion, as indicated by the selected intermolecular distances less than 3.5 Å which are shown in Table IX. The rms displacements for the thermal ellipsoids in this molecule are presented in Table X.[16]

$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ consists of discrete distorted octahedral $[Cr(en)_3]^{3+}$ and $[MoO(OH)(CN)_4]^{3-}$ ions. The negative ion consists of a nearly linear trans arrangement of the coordinated oxygen atoms (the O–Mo–O angle is 174.0 (4)°) in which the molybdenum lies randomly on either side of the center of symmetry. The ions are associated by hydrogen bonding as indicated by the selected intermolecular distances less than 3.5 Å which are given in Table XI. The rms displacements for the thermal ellipsoids are shown in Table XII.[16]

Table XI. Selected Interionic Distances Less Than 3.5 Å for $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$

Distance	Value, Å	Distance	Value, Å
O(1)-N(4)	2.945 (6)	O(2)-N(2)	2.87 (1)
O(1)-N(5)	2.876 (7)	N(1)-N(3)	3.436 (9)
O(1)-N(5)[a]	2.871 (8)	N(2)-N(3)	3.492 (6)
O(2)-N(1)	3.04 (1)		

Discussion

Comparisons of bond distances found in these structure determinations with those previously reported are outlined in Table XIII.

$[Pt(en)_2]^{2+}$. A previous determination of the structure of the $[Pt(en)_2]^{2+}$ ion was not found. However, the structure of *trans*-$[Pt(en)_2Cl_2]Cl_2$[19] is available for comparison. The Pt–N distances in the six-coordinate Pt(IV) complex are somewhat longer than those found by us, as are the Pt–N distances reported for $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$.[20] The longer distances in the tetraammine complex might be explained in terms of the relatively weaker bonding of ammonia when compared with ethylenediamine. The wide variation in C–N distances (1.42–1.59 Å) for $[Pt(en)_2]^{2+}$ can be rationalized in at least three ways. (1) The disordered ethylenediamine carbons have an electron density of about 3% of that of the nearby platinum, and therefore small errors in calculating the anomalous dispersion effects for Pt or errors which certainly exist in the correction of the data for absorption could result in systematic errors for the positional parameters of these carbons. (2) One of the two positions taken by these carbon atoms could be preferred due to packing effects in the crystal. The resulting difference in electron densities for the two sites could be reflected in positional parameters which are distorted to correct for this difference. (3) The nitrogen atom (N(3)) which is bonded to the troublesome half carbon atoms is hydrogen bonded (Table XI), which may affect the location of this atom in a way that affects the C–N distances. The mean C–N bond length in $[Pt(en)_2]^{2+}$, 1.50 (1) Å, agrees well with that reported for *trans*-$[Pt(en)_2Cl_2]Cl_2$[19] and with that found for EDTA.[21] These distances also compare favorably with those reported for $[Cr(en)_3]^{3+}$ (this work and ref 22). C–C distances in $[Pt(en)_2]^{2+}$ and in $[Cr(en)_3]^{3+}$ are the same within experimental error, and they are strikingly like those reported previously for *trans*-$[Pt(en)_2Cl_2]Cl_2$,[19] $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$,[22] and EDTA.[21]

$[Cr(en)_3]^{3+}$. The bond distances found for this ion are in excellent agreement with those found for the same ion in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$.[22] The ethylenediamine bonds agree well with those found for $[Pt(en)_2]^{2+}$, as was mentioned above.

$[MoO(OH_2)(CN)_4]^{2-}$ and $[MoO(OH)(CN)_4]^{3-}$. Mo–C distances are 2.150 (8)–2.105 (6) Å in the diprotonated complex and 2.10 (1)–2.25 (1) Å for the monoprotonated complex. The wide variation for the monoprotonated complex is most likely due to the fact that the reported positional parameters do not include two different positions for the cyanide atoms, which would be necessary for the maintenance of a linear Mo–CN arrangement when the molybdenum atom takes two positions. Disordered nitrogens were not reported due to the questionability of attempting to refine atom positions which are less than 0.2 Å apart. A wide range of Mo–C distances has also been reported for $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$.[3] The Mo–C distances in $K_4[Mo(CN)_8]\cdot 2H_2O$[23] agree very well with those found for $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ and with the mean value of those found for

Table XIII. Comparison of Bond Distances with Those Reported Previously

Bond	Distance	Compd	Ref
Pt–N	2.024 (4)–2.036 (4)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	2.045 (16)–2.068 (17)	*trans*-$[Pt(en)_2Cl_2]Cl_2$	19
	2.047 (9)–2.059 (9)	$[Pt(NH_3)_4[Re_2O_3(CN)_8]$	20
Cr–N	2.061 (5)–2.080 (4)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	2.062 (7)–2.083 (7)	$[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$	22
C–N	1.42 (1)–1.59 (2)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	1.468 (28)–1.521 (3)	*trans*-$[Pt(en)_2Cl_2]Cl_2$	19
	1.491 (6)–1.504 (7)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	1.461 (11)–1.503 (12)	$[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$	22
	1.497 (2)–1.508 (2)	EDTA	21
C–C	1.48 (1)–1.53 (2)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	1.53 (3)	*trans*-$[Pt(en)_2Cl_2]Cl_2$	19
	1.48 (1)–1.505 (8)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	1.489 (13)–1.518 (14)	$[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$	21
	1.512 (2)–1.526 (2)	EDTA	21
Mo–C	2.150 (8)–2.166 (6)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	2.10 (1)–2.25 (1)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	2.189 (12)–2.220 (13)	$NaK_3[MoO_2(CN)_4]\cdot 6H_2O$	3
	2.154 (8)–2.172 (8)	$K_4[Mo(CN)_8]\cdot 2H_2O$	23
C≡N	1.141 (7)–1.143 (6)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	1.130 (6)–1.139 (7)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	1.150 (17)–1.186 (16)	$NaK_3[MoO_2(CN)_4]\cdot 6H_2O$	3
	1.136 (10)–1.166 (11)	$K_4[Mo(CN)_8]\cdot 2H_2O$	23
	1.154 (5)–1.156 (5)	$K_3[ReO_2(CN)_4]$	24
	1.130 (9)–1.137 (9)	$[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$	22
$Mo-OH_2$	2.271 (4)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	2.281 (3)–2.283 (3)	$MoO_3\cdot 2H_2O$	23
Mo–OH	2.077 (7)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	2.181 (3)	$MoO_3\cdot 2H_2O$	23
	1.96 (1)	$Mo_4O_{10}(OH)_2$	24
$Mo-O_{bridging}$	1.963 (3)–2.311 (6)	$Mo_4O_{11.2}F_{0.8}$	24
	2.228 (4)–2.230 (4)	$HgMoO_4$	26
Mo–O	1.668 (5)	$[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$	This work
	1.698 (7)	$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$	This work
	1.834 (9)	$NaK_3[MoO_2(CN)_4]\cdot 6H_2O$	1
	1.683 (3)–1.722 (3)	$MoO_3\cdot 2H_2O$	23
	1.670; 1.684	$MoOCl_4$; $WOCl_4$	27
$Re-OH_2$	2.32 (4)	$(C_2H_5)_4N[ReO(OH_2)Br_4]$	28
$Re-O_{bridging}$	1.9149 (4)	$[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$	18
Re–O	1.781 (3)	$K_3[ReO_2(CN)_4]$	22
	1.71 (4)	$(C_2H_5)_4N[ReO(OH_2)Br_4]$	28
	1.698 (7)	$[Pt(NH_3)_4]_2[Re_2O_3(CN)_4]$	18

$[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$. The C≡N distances found for these compounds agree well with those published previously, as shown in Table XIII.[20,23,24] Table XIII also shows good agreement between previous determinations of the various Mo–O bonds.[1,25–29] Essentially three different molybdenum–oxygen bonds were found in this study: the rather long $Mo-OH_2$ bond (2.271 (4) Å), the Mo–OH bond (2.077 (7) Å), and the Mo–O bonds (1.698 (7) and 1.668 (5)Å). An intermediate bond (1.834 (9) Å) was found for $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$.[3] This trend can be explained in terms of the protonating of $[MoO_2(CN)_4]^{4-}$ (Mo–O distance 1.834 (9) Å) which weakens one Mo–O bond (2.077 (7) Å) and strengthens the other (1.698 (7) Å). Protonating the $[MoO(OH)(CN)_4]^{3-}$ complex ion increases the differences in bond strengths. The change in bond lengths for the second protonation is greater for the protonated oxygen (~0.2 Å) than it is for the nonprotonated oxygen (~0.03 Å). This same trend is found for the chemically similar and isoelectronic rhenium complexes.[20,24,30] The $Re-OH_2$ bond[30] was found to be 2.32 (4) Å, the $Re-O_{bridging}$ bond[20] was reported as 1.9149 (4) Å, and the Re–O bonds for the noncentric complexes were determined to be 1.698 (7)[20] and 1.71 (4) Å.[30] The Re–O bond in the dioxo complex is 1.781 (3) Å.[24] Because one of these complexes $[ReO(OH_2)Br_4]^-$ contains Br^- ions rather than CN^- ions, absolute values cannot be compared, only the general trends.

While the molybdenum and rhenium systems are the only two of this type to have been studied in some detail, the similar chemistry of these systems to that of other systems may indicate that the structures of ions in other systems (i.e., $[OsO_2X_4]^{2-}$, $[WO_2X_4]^{4-}$) may also be similar and that the diprotonated forms of these complexes may also be in the aquooxo form rather than in the dihydroxy form.

If one assumes the solid structures represent the species in solution, then it has been shown that hydrolysis of $[MoO_2(CN)_4]^{4-}$ can be described by the equations

$$MoO_2(CN)_4{}^{4-} + H_2O \rightleftharpoons MoO(OH)(CN)_4{}^{3-} + OH^-$$

$$MoO(OH)(CN)_4{}^{3-} + H_2O \rightleftharpoons MoO(H_2O)(CN)_4{}^{2-} + OH^-$$

The solid structures of these two blue products have been determined, and it has been shown that the diprotonated complex has the oxoaquo and not the dihydroxo structure. The previously reported green compound found in the pH 7–5 region has been characterized as a mixture of the oxoaquo complex and a tannish colloidal product containing no cyanide ion. No evidence was found for dimerization of the oxohydroxo complex to a $O-Mo(CN)_4-O-Mo(CN)_4-O^{6-}$ ion such as was found with the analogous Re(V) complex ion.[20]

Registry No. $K_4[MoO_2(CN)_4]$, 22724-02-3; $K_3[MoO(OH)(CN)_4]$, 55493-42-0; $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$, 55493-44-2; $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$, 55493-47-5.

Supplementary Material Available. Listings of structure factor amplitudes and Tables I, III, X, and XII showing hydrogen atom positions and rms components of thermal displacement along the principal axes 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 AIC50064C-9-75.

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Molecules with an M_4X_4 Core. V.[1-4] Crystallographic Characterization of the Tetrameric "Cubane-Like" Species Triethylphosphinecopper(I) Chloride and Triethylphosphinecopper(I) Bromide. Systematics in the $[PEt_3CuX]_4$ Series

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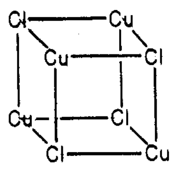
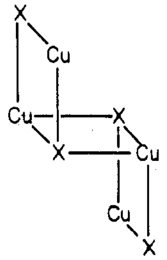
The tetrameric species triethylphosphinecopper(I) chloride, $[PEt_3CuCl]_4$, and triethylphosphinecopper(I) bromide, $[PEt_3CuBr]_4$, have been synthesized and their molecular parameters determined *via* single-crystal X-ray diffraction studies. Each crystallizes in the noncentrosymmetric polar space group $I\bar{4}3m$ (T_d^3; No. 217) with $Z = 2$. X-Ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer. Unit cell constants are $a = 12.5924$ (18) Å for $[PEt_3CuCl]_4$ and $a = 12.7495$ (18) Å for $[PEt_3CuBr]_4$. All atoms were located, final discrepancy indices being $R_F = 2.10\%$ and $R_{wF} = 2.41\%$ for $[PEt_3CuCl]_4$ and $R_F = 1.81\%$ and $R_{wF} = 1.73\%$ for $[PEt_3CuBr]_4$. Each of the tetrameric molecules lies on a site of T_d ($\bar{4}3m$) symmetry with methylene groups and methyl hydrogens disordered about crystallographic mirror planes. The four copper and four halogen atoms, taken alternately, define a "cubane-like" arrangement in which Cu–(μ_3-Cl) = 2.4383 (10) Å and Cu–(μ_3-Br) = 2.5436 (8) Å. Intramolecular Cu···Cu distances are 3.2111 (16) Å for $[PEt_3CuCl]_4$ and 3.1836 (18) Å for $[PEt_3CuBr]_4$; intramolecular halogen···halogen contacts are close to the sum of their van der Waals radii, with Cl···Cl = 3.6567 (22) Å and Br···Br = 3.9324 (13) Å. The completion of these two structural studies allows a detailed comparison of molecular parameters in the isomorphous and isostructural series $[PEt_3CuX]_4$ (X = Cl, Br, I).

Introduction

We have recently completed a series of X-ray diffraction studies on the tetrameric triphenylphosphinecopper(I) halides $[PPh_3CuX]_4$ (X = Cl,[1] Br,[2] I[4]). The most important result from this work was the discovery that the Cu_4Cl_4 core of $[PPh_3CuCl]_4$ has the well-known "cubane-like" stereochemistry (see structure I) whereas the Cu_4X_4 cores of both $[PPh_3CuBr]_4$ and $[PPh_3CuI]_4$ have "step" structures (see structure II). A secondary result was an indication that, regardless of the gross molecular configuration, the geometry of the individual four-membered Cu_2X_2 rings which constitute each of the structures is dictated primarily by interatomic repulsions.



I



II

The "step" structure has been found only in those $[PR_3CuX]_4$ species which contain both bulky phosphine ligands and large halogen atoms. Thus $[PEt_3CuI]_4$ has been shown to have a "cubane-like" Cu_4I_4 core (see structure III).

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