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# The Identification and Structural Characterization of $[enH_2]_2[Mo_2Cl_8]\cdot 2H_2O$, a Compound Containing the Octachlorodimolybdate(II) Ion[1]

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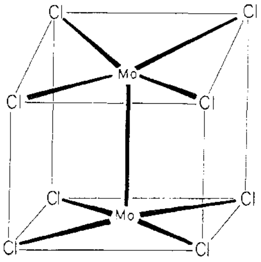
The violet compound $[enH_2]_2[Mo_2Cl_8]\cdot 2H_2O$ ($enH_2 = H_3NCH_2CH_2NH_3^{2+}$) was prepared by treatment of $Mo_2(O_2CCH_3)_4$ with a solution of $[enH_2]Cl_2$ in 6 *M* aqueous HCl at 0°. Crystallographic data are: $P2_1/c$; $Z = 2$; $a = 8.214 \pm 0.003$ Å, $b = 15.976 \pm 0.005$ Å; $c = 8.486 \pm 0.003$ Å; $\beta = 118.08 \pm 0.03°$; $d(\text{calcd}) = 2.15$ g cm$^{-3}$; $d(\text{obsd}) = 2.12 \pm 0.04$ g cm$^{-3}$. The 1225 independent reflections within the sphere bounded by $\theta = 55°$ were collected on a counter diffractometer, using Cu K$\alpha$ radiation. The structure was solved by symbolic addition and difference synthesis. Full-matrix, anisotropic least-squares refinement, including corrections (to 32 reflections) for secondary extinction and including H atoms, led to final unweighted and weighted residuals of 0.040 and 0.055, respectively. The $Mo_2Cl_8^{4-}$ ion, of crystallographic symmetry $C_i$, is a nearly cubic square parallelepiped (square base edges, 3.35 Å; vertical edges, 3.41 Å). The pair of Mo atoms lie along the approximate fourfold axis, separated by 2.134 (1) Å. The Mo–Cl distances are all in the range 2.45 ± 0.01 Å and the most acute Cl–Mo–Cl angles are all in the range 85.5–87.0°. The dimensions of the $H_3NCH_2CH_2NH_3^{2+}$ ion are all normal. The infrared spectrum suggests that the O–H bonds of the water molecule are only weakly involved in hydrogen bonding and this is confirmed by the structural parameters (shortest O–H···Cl distances in the range 3.27–3.38 Å).

## Introduction

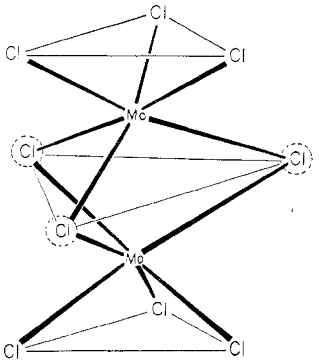
Investigations carried out in this laboratory[3-5] and by Sheldon and his coworkers[6,7] had shown that by treatment of dimolybdenum tetraacetate with aqueous hydrohalic acids, various products could be obtained, some of which were reasonably suspected of having Mo–Mo bonds.

In two cases, X-ray study of crystalline compounds has led to identification of dinuclear chloro anions and detailed structural characterization of them. We first isolated[3] the red crystalline compound $K_4Mo_2Cl_8\cdot 2H_2O$, which does not seem to be exactly the same as any substance described by Sheldon, although in color it resembles Anderson and Sheldon's "$K_6Mo_3Cl_{12}$." X-Ray study of $K_4Mo_2Cl_8\cdot 2H_2O$ demonstrated the existence of the $Mo_2Cl_8^{4-}$ ion, with structure I, which has the same geometry (idealized symmetry $D_{4h}$) as the $Re_2Cl_8^{2-}$ ion with which it is isoelectronic.



I

In a second paper[4] we have shown that the golden yellow compound $Cs_3Mo_2Cl_8$, described by Anderson and Sheldon as $Cs_6Mo_4Cl_{16}$, and its rubidium analog are isomorphous. A single-crystal study of $Rb_3Mo_2Cl_8$ showed that this is indeed the true molecular formula and that the $Mo_2Cl_8^{3-}$ ion has the structure of a confacial bioctahedron with one empty bridge position, II.



II

In the present report we describe the preparation and structural characterization of the violet compound $[enH_2]_2[Mo_2Cl_8]\cdot 2H_2O$. On the basis of color and method of preparation, this seems virtually certain to be the same substance as the one to which Allison, Anderson, and Sheldon[7] assigned the formula $[enH_2]_3Mo_3Cl_{13}(H_3O)(H_2O)_2$ and proposed that it contains a trinuclear, triangular cluster of Mo atoms. We have established conclusively that the microcrystalline powder which is the first reaction product when $Mo_2(O_2CCH_3)_4$ is treated with an approximately 6 *M* HCl solution of $[enH_2]Cl_2$ is identical with the substance making up the larger crystals which were obtained by recrystallization and used in a single-crystal X-ray study of the structure.

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(3) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

(4) J. V. Brencic and F. A. Cotton, *ibid.*, **8**, 1060 (1969).

(5) J. V. Brencic and F. A. Cotton, studies of the chemistry and structures of other low-valent molybdenum compounds obtained directly or in several steps from $Mo_2(O_2CCH_3)_4$, to be submitted for publication.

(6) I. R. Anderson and J. C. Sheldon, *Australian J. Chem.*, **18**, 271 (1965).

(7) G. B. Allison, I. R. Anderson, and J. C. Sheldon, *ibid.*, **20**, 869 (1967).

The X-ray work proves that the correct formula is $[enH_2^{2+}]_2[Mo_2Cl_8^{4-}]\cdot 2H_2O$ and shows that the molybdenum-containing complex anion is the same $Mo_2Cl_8^{4-}$ ion, I, previously described.[3] Thus, we have now determined the structures of red, violet, and yellow compounds obtained by treatment of $Mo_2(O_2CCH_3)_4$ with aqueous HCl under various conditions and in each of the three cases, only dinuclear complex anions have been found.

Although no new molybdenum cluster species was found in $[enH_2]_2[Mo_2Cl_8]\cdot 2H_2O$, the thorough refinement of this structure was considered worthwhile in order to determine the constancy of the dimensions of the $Mo_2Cl_8^{4-}$ ion and to improve the accuracy with which these dimensions, especially the Mo–Mo bond length, are known. In $K_4Mo_2Cl_8\cdot 2H_2O$, there was a disordering of $Mo_2$ units within the $Cl_8$ cages to the extent of about 7%. This introduced a degree of uncertainty which was not easy to estimate with precision into the dimensions of the $Mo_2Cl_8^{4-}$ group. In the present compound no such problems were encountered and the dimensions now available have only small and well-established uncertainty intervals.

## Experimental Section

**Preparation.**—Constant-boiling hydrochloric acid (200 ml) at 0°, dimolybdenum tetraacetate (4.0 g), and ethylenediamine dihydrochloride (2.9 g) were mixed and stirred under prepurified nitrogen at 0° for 1 hr. The violet, microcrystalline precipitate was collected on a filter and washed with two portions (20 ml each) of absolute ethanol and two portions (20 ml each) of ether. The substance was then dried under vacuum at 25° for 2 hr; yield, 4.0 g (70% based on $Mo_2(O_2CCH_3)_4$). *Anal.* Calcd for $C_4H_{24}N_4O_2Cl_8Mo_2$: C, 7.55; H, 3.81; N, 8.81; Cl, 44.61; Mo, 30.19. Found: C, 7.60; H, 3.69; N, 8.55; Cl, 44.6; Mo, 29.7. Chlorine was determined by the Volhard method and molybdenum as lead molybdate. C, H, and N were determined by standard microanalytic procedures.

Larger crystals, suitable for single-crystal X-ray work, were obtained in the following way. A solution of 1.09 g of the microcrystalline product in 50 ml of constant-boiling hydrochloric acid at room temperature was prepared. A solution of 2.0 g of ethylenediamine dihydrochloride, $[enH_2]Cl_2$, in 50 ml of the same solvent was added to it and the combined solution was kept at 0° for 24 hr. In this way well-formed crystals having dimensions of about 0.5 mm were produced.

The identity of the microcrystalline substance and the larger crystals was substantiated in two ways. First a sample made up entirely of larger crystals was shown to have the same chemical analysis as the microcrystalline powder. Second, the powder diffraction pattern of the microcrystalline substance was found to be completely consistent with the unit cell dimensions and space group of the larger single crystals.

The density of the larger crystals was determined by flotation in a mixture of iodomethane and carbon tetrachloride, giving a value of $2.12 \pm 0.04$ g cm$^{-3}$. That calculated from the dimensions and content of the unit cell (*vide infra*) is 2.15 g cm$^{-3}$.

The infrared spectrum was recorded on a Beckman 337 spectrometer from 2.5 to 16 $\mu$, using a mineral oil mull between rock salt plates. Besides bands due to the $H_3NCH_2CH_2NH_3^{2+}$ groups, there are strong and fairly sharp bands at 3540 and 3480 cm$^{-1}$, assignable to O–H stretching, and a sharp band of medium intensity at 1600 cm$^{-1}$ which we would assign to the bending mode of the $H_2O$ molecule. The sharpness and high energy of the O–H stretching bands indicates that there is only weak O–H···Cl hydrogen bonding,[8–10] and this is confirmed by the structure determination.

The compound appeared to be stable in air throughout all of the measurements just described and during other lengthy periods of exposure, up to several months.

A magnificently formed, rhomboidal crystal was selected for the X-ray study. Examination in polarized light showed that it was birefringent. The six faces of this crystal (as later identified) were $\bar{1}1\bar{1}$, $1\bar{1}1$, $1\bar{1}\bar{1}$, $\bar{1}11$, 001, and $00\bar{1}$. The diagonals of the 001 and $00\bar{1}$ faces were 0.08 and 0.16 mm while the thickness of the crystal perpendicular to these faces was 0.06 mm.

Weissenberg and precession photographs taken with unfiltered Cu K$\alpha$ radiation showed that the lattice is monoclinic. Systematic absences ($l \neq 2n$ for $h0l$, $k \neq 2n$ for $0k0$) showed that the likely space group is $P2_1/c$, a result confirmed by the successful structure analysis. Accurate values of the unit cell dimensions were obtained by measuring, at 24 ± 1°, the positions of 30 reflections in the $h00$, $0k0$, $00l$, and $h0l$ sets on a General Electric XRD-5 counter diffractometer equipped with a quarter-circle eucentric goniometer. These data were treated by least squares, with standard deviations being obtained from diagonal elements of the inverse matrix. The results are: $a = 8.214 \pm 0.003$ Å; $b = 15.976 \pm 0.005$ Å; $c = 8.486 \pm 0.003$ Å; $\beta = 118.08 \pm 0.03°$.

Using a manually operated GE XRD-5 counter diffractometer equipped with a quarter-circle eucentric goniometer, 1225 independent reflections within a sphere in reciprocal space bounded by $\theta = 55°$ were collected. Copper K$\alpha$ radiation filtered through nickel foil in the incident beam was used and the crystal was mounted along the $b$ axis. Each peak was scanned from $2\theta$ (calcd) − 1.33° to $2\theta$ (calcd) + 1.33° at a scan rate of 4°/min, giving $P$ counts. Background was counted for 20 sec each at the beginning ($B_1$) and end ($B_2$) of each scan. The intensity, $I$, was then taken as $I = P - B_1 - B_2$. When the value of $I$ was $\leq 0$ for a given reflection, it was measured at least four times and averages for peak and background were used. When $I$ was still measured as $\leq 0$, it was estimated as $^1/_2(P + B_1 + B_2)^{1/2}$. Structure factors on a relative scale were obtained by applying Lorentz, polarization, and absorption corrections to the measured intensities, *viz.*, $|F_o| = [I/ALp]^{1/2}$. The standard deviation, $\sigma$, of an $I$ value was taken as $(P + B_1 + B_2)^{1/2}$. The standard deviation, $\sigma(F)$, applicable to each observed structure amplitude was determined from the expression: $\sigma(F) = [\sigma^2 + pI^2]^{1/2}/2ALp|F_o|$, with $p = 0.002$. During the process of intensity measurement six standard reflections were checked twice a day. No significant changes or trends were observed. Reflections (13) with peak count >20,000 were remeasured at a lower current. The lowering in the peak count was proportional to the change in the current value to the same extent for all reflections.

Reflections in the $0k0$ series showed variations from 100 to 55 in the peak count on a relative scale during rotation about the $\phi$ axis at $\chi = 90°$. After application of an absorption correction ($\mu = 208.2$ cm$^{-1}$) this variation was reduced to the range from 100 to 86. Transmission factors, $A$, for the whole set of data varied from 0.251 to 0.490

## Solution and Refinement[11]

The structure was solved using the symbolic addition procedure to apply the Karle–Hauptman Sigma-2 relationship.[12] The programs FAME and MAGIC by R. Dewar and A. Stone of the University of Chicago were employed in a local version suitable for the IBM 360

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[8] A comparison may be made with the case of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ where the infrared spectrum (sharp, strong bands at 3640, 3560, and 1615 cm$^{-1}$) was interpreted to show that the water molecules in this substance form no strong hydrogen bonds.[9] An X-ray study[10] subsequently confirmed this.

[9] F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).

[10] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

[11] For a listing of the computer programs used in processing data, solving and refining the structure, and computing molecular dimensions, see F. A. Cotton and B. M. Foxman, *ibid.*, **7**, 1784 (1968).

[12] J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

TABLE I

OBSERVED AND FINAL CALCULATED STRUCTURE FACTORS IN UNITS OF 0.1 ELECTRON

| H | L | FOBS | FCAL |
|---|---|---|---|
| **K = 0**** | | | |
| 1 | 0 | 1243 | 1139 |
| 2 | 0 | 809 | 801 |
| 3 | 0 | 1398 | 1356 |
| 4 | 0 | 150 | 186 |
| 5 | 0 | 468 | 427 |
| 6 | 0 | 308 | 312 |
| 7 | 0 | 297 | 292 |
| 0 | 2 | 369 | 326 |
| -1 | 2 | 1095 | 1038 |
| 1 | 2 | 1313 | 1296 |
| 2 | 2 | 809 | 768 |
| -2 | 2 | 194 | 194 |
| -3 | 2 | 856 | 847 |
| 3 | 2 | 643 | 613 |
| -4 | 2 | 1710 | 1699 |
| 4 | 2 | 791 | 307 |
| -5 | 2 | 525 | 537 |
| 5 | 2 | 433 | 432 |
| -6 | 2 | 788 | 797 |
| 6 | 2 | 698 | 708 |
| -7 | 2 | 547 | 548 |
| -8 | 2 | 244 | 226 |
| 0 | 4 | 1461 | 1433 |
| -1 | 4 | 1332 | 1358 |
| 1 | 4 | 932 | 953 |
| -2 | 4 | 344 | 302 |
| 2 | 4 | 812 | 823 |
| 3 | 4 | 368 | 387 |
| -3 | 4 | 370 | 288 |
| 4 | 4 | 627 | 645 |
| -4 | 4 | 307 | 295 |
| 5 | 4 | 372 | 394 |
| -5 | 4 | 394 | 381 |
| -6 | 4 | 363 | 367 |
| -7 | 4 | 714 | 728 |
| -8 | 4 | 418 | 436 |
| 0 | 6 | 1262 | 1259 |
| -1 | 6 | 682 | 672 |
| 1 | 6 | 1118 | 1148 |
| -2 | 6 | 695 | 653 |
| 2 | 6 | 340 | 329 |
| -3 | 6 | 722 | 710 |
| 3 | 6 | 446 | 452 |
| -4 | 6 | 1186 | 1257 |
| -5 | 6 | 655 | 650 |
| -6 | 6 | 127 | 111 |
| -7 | 6 | 348 | 348 |
| -8 | 6 | 127 | 112 |
| -1 | 8 | 50 | 12 |
| -2 | 8 | 177 | 160 |
| -3 | 8 | 1031 | 1051 |
| -4 | 8 | 727 | 739 |
| -5 | 8 | 708 | 695 |
| -6 | 8 | 578 | 596 |
| -7 | 8 | 313 | 318 |
| **K = 1**** | | | |
| 1 | 0 | 8 | 16 |
| 2 | 0 | 27 | 14 |
| 3 | 0 | 897 | 897 |
| 4 | 0 | 611 | 620 |
| 5 | 0 | 227 | 212 |
| 6 | 0 | 520 | 500 |
| 7 | 0 | 372 | 332 |
| 0 | 1 | 1163 | 1210 |
| -1 | 1 | 1239 | 1182 |
| 1 | 1 | 896 | 885 |
| -2 | 1 | 1114 | 1070 |
| 2 | 1 | 456 | 416 |
| -3 | 1 | 2059 | 2024 |
| 3 | 1 | 350 | 341 |
| -4 | 1 | 1162 | 1227 |
| 4 | 1 | 462 | 463 |
| 5 | 1 | 298 | 283 |
| -5 | 1 | 551 | 524 |
| 6 | 1 | 572 | 569 |
| -6 | 1 | 229 | 236 |
| 7 | 1 | 447 | 471 |
| -7 | 1 | 475 | 461 |
| -8 | 1 | 74 | 8 |
| 0 | 2 | 573 | 546 |
| -1 | 2 | 172 | 180 |
| 1 | 2 | 524 | 509 |
| 2 | 2 | 343 | 284 |
| -2 | 2 | 459 | 459 |
| -3 | 2 | 653 | 639 |
| 3 | 2 | 176 | 163 |
| -4 | 2 | 320 | 324 |
| 4 | 2 | 64 | 23 |
| -5 | 2 | 43 | 24 |
| 5 | 2 | 367 | 353 |
| -6 | 2 | 545 | 531 |
| 6 | 2 | 137 | 123 |
| -7 | 2 | 481 | 466 |
| -8 | 2 | 144 | 147 |
| 0 | 3 | 307 | 298 |
| -1 | 3 | 340 | 337 |
| 1 | 3 | 41 | 23 |
| -2 | 3 | 998 | 989 |
| 2 | 3 | 856 | 886 |
| 3 | 3 | 1067 | 1122 |
| -3 | 3 | 550 | 561 |
| -4 | 3 | 928 | 948 |
| 4 | 3 | 802 | 817 |
| -5 | 3 | 204 | 196 |
| 5 | 3 | 595 | 620 |
| -6 | 3 | 250 | 235 |
| -7 | 3 | 1065 | 1061 |
| -8 | 3 | 457 | 479 |
| 0 | 4 | 95 | 84 |
| -1 | 4 | 314 | 265 |
| 1 | 4 | 350 | 350 |
| -2 | 4 | 192 | 172 |
| 2 | 4 | 287 | 290 |
| 3 | 4 | 365 | 373 |
| -3 | 4 | 185 | 165 |
| 4 | 4 | 116 | 93 |
| -4 | 4 | 297 | 315 |
| 5 | 4 | 181 | 161 |
| -5 | 4 | 195 | 173 |
| -6 | 4 | 114 | 97 |
| -7 | 4 | 120 | 60 |
| -8 | 4 | 182 | 157 |
| 0 | 5 | 593 | 577 |
| -1 | 5 | 1306 | 1316 |
| 1 | 5 | 743 | 735 |
| -2 | 5 | 688 | 678 |
| 2 | 5 | 457 | 470 |
| -3 | 5 | 607 | 606 |
| 3 | 5 | 383 | 384 |
| 4 | 5 | 689 | 710 |
| -4 | 5 | 1085 | 1143 |
| -5 | 5 | 64 | 35 |
| -6 | 5 | 533 | 527 |
| -7 | 5 | 551 | 668 |
| -8 | 5 | 684 | 684 |
| 0 | 6 | 157 | 137 |
| -1 | 6 | 187 | 173 |
| 1 | 6 | 134 | 146 |
| -2 | 6 | 73 | 65 |
| 2 | 6 | 145 | 138 |
| -3 | 6 | 636 | 620 |
| -4 | 6 | 215 | 210 |
| -5 | 6 | 265 | 264 |
| -6 | 6 | 501 | 498 |
| -7 | 6 | 425 | 421 |
| -8 | 6 | 469 | 450 |
| 0 | 7 | 763 | 762 |
| -1 | 7 | 428 | 442 |
| 1 | 7 | 274 | 279 |
| -2 | 7 | 1013 | 1014 |
| -3 | 7 | 1021 | 1013 |
| -4 | 7 | 588 | 585 |
| -5 | 7 | 520 | 519 |
| -6 | 7 | 30 | 19 |
| -7 | 7 | 364 | 355 |
| -8 | 7 | 385 | 385 |
| -1 | 8 | 50 | 21 |
| -2 | 8 | 84 | 37 |
| -3 | 8 | 129 | 115 |
| -4 | 8 | 17 | 17 |
| -5 | 8 | 57 | 17 |
| -6 | 8 | 346 | 335 |
| -7 | 8 | 293 | 288 |
| -4 | 9 | 117 | 115 |
| **K = 2**** | | | |
| 0 | 0 | 1307 | 1457 |
| 1 | 0 | 1071 | 1047 |
| 2 | 0 | 634 | 615 |
| 3 | 0 | 206 | 160 |
| 4 | 0 | 276 | 291 |
| 5 | 0 | 61 | 10 |
| 6 | 0 | 299 | 268 |
| 7 | 0 | 274 | 265 |
| 0 | 1 | 249 | 193 |
| 1 | 1 | 419 | 455 |
| -1 | 1 | 260 | 268 |
| -2 | 1 | 346 | 344 |
| 2 | 1 | 290 | 287 |
| -3 | 1 | 1027 | 1036 |
| 3 | 1 | 981 | 1053 |
| -4 | 1 | 671 | 704 |
| 4 | 1 | 811 | 783 |
| 5 | 1 | 589 | 572 |
| -5 | 1 | 216 | 191 |
| 6 | 1 | 156 | 154 |
| -6 | 1 | 627 | 604 |
| 7 | 1 | 181 | 146 |
| -7 | 1 | 870 | 858 |
| -8 | 1 | 378 | 410 |
| 0 | 2 | 197 | 184 |
| -1 | 2 | 266 | 271 |
| 1 | 2 | 835 | 780 |
| 2 | 2 | 154 | 133 |
| -2 | 2 | 346 | 344 |
| -3 | 2 | 731 | 729 |
| 3 | 2 | 761 | 772 |
| -4 | 2 | 1035 | 1089 |
| 4 | 2 | 425 | 413 |
| -5 | 2 | 815 | 828 |
| 5 | 2 | 816 | 806 |
| -6 | 2 | 1095 | 1063 |
| 6 | 2 | 792 | 817 |
| -7 | 2 | 566 | 562 |
| -8 | 2 | 261 | 233 |
| 0 | 3 | 715 | 699 |
| -1 | 3 | 764 | 790 |
| 1 | 3 | 275 | 251 |
| -2 | 3 | 821 | 833 |
| 2 | 3 | 36 | 33 |
| 3 | 3 | 164 | 173 |
| -3 | 3 | 701 | 692 |
| -4 | 3 | 725 | 732 |
| 4 | 3 | 355 | 372 |
| -5 | 3 | 280 | 274 |
| 5 | 3 | 99 | 88 |
| -6 | 3 | 131 | 121 |
| -7 | 3 | 415 | 385 |
| -8 | 3 | 190 | 184 |
| 0 | 4 | 733 | 738 |
| -1 | 4 | 1089 | 1088 |
| 1 | 4 | 730 | 718 |
| -2 | 4 | 308 | 294 |
| 2 | 4 | 829 | 835 |
| -3 | 4 | 529 | 548 |
| 3 | 4 | 242 | 242 |
| 4 | 4 | 443 | 448 |
| -4 | 4 | 764 | 783 |
| 5 | 4 | 305 | 341 |
| -5 | 4 | 919 | 953 |
| -6 | 4 | 556 | 577 |
| -7 | 4 | 870 | 871 |
| -8 | 4 | 421 | 416 |
| 0 | 5 | 69 | 40 |
| -1 | 5 | 206 | 215 |
| 1 | 5 | 161 | 148 |
| -2 | 5 | 694 | 703 |
| 2 | 5 | 385 | 385 |
| -3 | 5 | 477 | 473 |
| 3 | 5 | 447 | 467 |
| 4 | 5 | 445 | 478 |
| -4 | 5 | 788 | 809 |
| -5 | 5 | 540 | 570 |
| -6 | 5 | 61 | 29 |
| -7 | 5 | 838 | 841 |
| -8 | 5 | 472 | 465 |
| 0 | 6 | 468 | 462 |
| -1 | 6 | 334 | 330 |
| 1 | 6 | 709 | 705 |
| -2 | 6 | 446 | 394 |
| 2 | 6 | 255 | 262 |
| -3 | 6 | 81 | 26 |
| -4 | 6 | 529 | 514 |
| -5 | 6 | 465 | 463 |
| -6 | 6 | 64 | 40 |
| -7 | 6 | 218 | 222 |
| -8 | 6 | 209 | 225 |
| 0 | 7 | 263 | 279 |
| -1 | 7 | 291 | 283 |
| 1 | 7 | 345 | 351 |
| -2 | 7 | 17 | 28 |
| -3 | 7 | 292 | 284 |
| -4 | 7 | 69 | 52 |
| -5 | 7 | 184 | 162 |
| -6 | 7 | 642 | 642 |
| -7 | 7 | 632 | 649 |
| -1 | 8 | 202 | 195 |
| -2 | 8 | 199 | 206 |
| -3 | 8 | 716 | 698 |
| -4 | 8 | 591 | 570 |
| -5 | 8 | 775 | 756 |
| -6 | 8 | 699 | 701 |
| -7 | 8 | 307 | 309 |
| **K = 3**** | | | |
| 1 | 0 | 392 | 388 |
| 2 | 0 | 227 | 204 |
| 3 | 0 | 984 | 1035 |
| 4 | 0 | 1062 | 1070 |
| 5 | 0 | 351 | 361 |
| 6 | 0 | 667 | 636 |
| 7 | 0 | 508 | 499 |
| 0 | 1 | 257 | 255 |
| 1 | 1 | 1255 | 1246 |
| -1 | 1 | 517 | 498 |
| -2 | 1 | 556 | 581 |
| 2 | 1 | 105 | 117 |
| -3 | 1 | 1103 | 1074 |
| 3 | 1 | 42 | 64 |
| -4 | 1 | 545 | 528 |
| 4 | 1 | 410 | 408 |
| 5 | 1 | 128 | 104 |
| -5 | 1 | 220 | 225 |
| 6 | 1 | 474 | 445 |
| -6 | 1 | 200 | 201 |
| 7 | 1 | 258 | 261 |
| -7 | 1 | 119 | 102 |
| 0 | 2 | 1776 | 1877 |
| -1 | 2 | 1227 | 1247 |
| 1 | 2 | 542 | 484 |
| 2 | 2 | 920 | 899 |
| -2 | 2 | 163 | 169 |
| -3 | 2 | 389 | 406 |
| 3 | 2 | 642 | 643 |
| -4 | 2 | 83 | 54 |
| 4 | 2 | 522 | 509 |
| -5 | 2 | 63 | 32 |
| 5 | 2 | 472 | 479 |
| -6 | 2 | 391 | 376 |
| 6 | 2 | 199 | 180 |
| -7 | 2 | 743 | 747 |
| -8 | 2 | 222 | 232 |
| 0 | 3 | 183 | 159 |
| -1 | 3 | 975 | 1010 |
| 1 | 3 | 350 | 366 |
| -2 | 3 | 763 | 771 |
| 2 | 3 | 888 | 920 |
| -3 | 3 | 255 | 268 |
| 3 | 3 | 763 | 766 |
| -4 | 3 | 740 | 746 |
| 4 | 3 | 539 | 568 |
| -5 | 3 | 532 | 527 |
| 5 | 3 | 622 | 638 |
| -6 | 3 | 580 | 587 |
| -7 | 3 | 595 | 575 |
| -8 | 3 | 413 | 551 |
| 0 | 4 | 690 | 680 |
| -1 | 4 | 636 | 633 |
| 1 | 4 | 979 | 1020 |
| -2 | 4 | 567 | 547 |
| 2 | 4 | 72 | 62 |
| -3 | 4 | 782 | 805 |
| 3 | 4 | 145 | 157 |
| -4 | 4 | 1373 | 1394 |
| 4 | 4 | 59 | 30 |
| -5 | 4 | 267 | [illegible] |
| -6 | 4 | 277 | 263 |
| -7 | 4 | 450 | 431 |
| -8 | 4 | 94 | 55 |
| 0 | 5 | 78 | 64 |
| -1 | 5 | 96 | 78 |
| 1 | 5 | 178 | 182 |
| -2 | 5 | 533 | 561 |
| 2 | 5 | 140 | 132 |
| -3 | 5 | 219 | 208 |
| 3 | 5 | 291 | 307 |
| -4 | 5 | 88 | 91 |
| -5 | 5 | 420 | 412 |
| -6 | 5 | 517 | 495 |
| -7 | 5 | 462 | 468 |
| -8 | 5 | 705 | 698 |
| 0 | 6 | 286 | 284 |
| -1 | 6 | 391 | 384 |
| 1 | 6 | 364 | 356 |
| -2 | 6 | 259 | 240 |
| 2 | 6 | 259 | 270 |
| -3 | 6 | 624 | 627 |
| -4 | 6 | 404 | 412 |
| -5 | 6 | 659 | 650 |
| -6 | 6 | 399 | 384 |
| -7 | 6 | 674 | 666 |
| -8 | 6 | 699 | 706 |
| 0 | 7 | 252 | 246 |
| -1 | 7 | 448 | 443 |
| 1 | 7 | 198 | 210 |
| -2 | 7 | 425 | 412 |
| -3 | 7 | 426 | 436 |
| -4 | 7 | 98 | 120 |
| -5 | 7 | 185 | 158 |
| -6 | 7 | 192 | 189 |
| -7 | 7 | 127 | 149 |
| -1 | 8 | 332 | 338 |
| -2 | 8 | 348 | 338 |
| -3 | 8 | 220 | 221 |
| -4 | 8 | 343 | 347 |
| -5 | 8 | 298 | 294 |
| -6 | 8 | 321 | 314 |
| **K = 4**** | | | |
| 0 | 0 | 16 | 32 |
| 1 | 0 | 720 | 771 |
| 2 | 0 | 514 | 501 |
| 3 | 0 | 101 | 48 |
| 4 | 0 | 444 | 431 |
| 5 | 0 | 339 | 340 |
| 6 | 0 | 105 | 98 |
| 7 | 0 | 103 | 94 |
| 0 | 1 | 1356 | 1383 |
| 1 | 1 | 517 | 512 |
| -1 | 1 | 275 | 274 |
| -2 | 1 | 582 | 581 |
| 2 | 1 | 1106 | 1160 |
| 3 | 1 | 1519 | 1479 |
| -3 | 1 | 231 | 238 |
| -4 | 1 | 531 | 508 |
| 4 | 1 | 551 | 545 |
| 5 | 1 | 830 | 795 |
| -5 | 1 | 326 | 333 |
| 6 | 1 | 261 | 279 |
| -6 | 1 | 677 | 667 |
| -7 | 1 | 673 | 660 |
| 0 | 2 | 126 | 126 |
| -1 | 2 | 408 | 426 |
| 1 | 2 | 322 | 305 |
| 2 | 2 | 273 | 278 |
| -2 | 2 | 205 | 217 |
| -3 | 2 | 32 | 78 |
| 3 | 2 | 218 | 203 |
| -4 | 2 | 115 | 119 |
| 4 | 2 | 211 | 201 |
| -5 | 2 | 646 | 630 |
| 5 | 2 | 645 | 638 |
| -6 | 2 | 676 | 672 |
| 6 | 2 | 376 | 381 |
| -7 | 2 | 262 | 270 |
| -8 | 2 | 100 | 49 |
| 0 | 3 | 1267 | 1233 |
| -1 | 3 | 1653 | 1733 |
| 1 | 3 | 1027 | 1055 |
| -2 | 3 | 1046 | 1050 |
| 2 | 3 | 982 | 985 |
| -3 | 3 | 1218 | 1255 |
| 3 | 3 | 239 | 245 |
| -4 | 3 | 1240 | 1215 |
| 4 | 3 | 532 | 529 |
| -5 | 3 | 291 | 277 |
| 5 | 3 | 189 | 200 |
| -6 | 3 | 88 | 95 |
| -7 | 3 | 362 | 337 |
| -8 | 3 | 331 | 338 |
| 0 | 4 | 279 | 273 |
| -1 | 4 | 214 | 220 |
| 1 | 4 | 564 | 543 |
| -2 | 4 | 55 | 39 |
| 2 | 4 | 337 | 349 |
| -3 | 4 | 154 | 142 |
| 3 | 4 | 24 | 6 |
| 4 | 4 | 73 | 60 |
| -4 | 4 | 633 | 647 |
| -5 | 4 | 833 | 869 |
| -6 | 4 | 124 | 119 |
| -7 | 4 | 67 | 18 |
| -8 | 4 | 66 | 70 |
| 0 | 5 | 381 | 370 |
| -1 | 5 | 203 | 199 |
| 1 | 5 | 437 | 425 |
| -2 | 5 | 1091 | 1128 |
| 2 | 5 | 378 | 382 |
| -3 | 5 | 899 | 930 |
| 3 | 5 | 293 | 317 |
| -4 | 5 | 638 | 639 |
| -5 | 5 | 725 | 731 |
| -6 | 5 | 378 | 371 |
| -7 | 5 | 500 | 483 |
| -8 | 5 | 333 | 332 |
| 0 | 6 | 53 | 55 |
| -1 | 6 | 113 | 89 |
| 1 | 6 | 168 | 174 |
| -2 | 6 | 161 | 150 |
| 2 | 6 | 330 | 326 |
| -3 | 6 | 105 | 80 |
| -4 | 6 | 145 | 150 |
| -5 | 6 | 243 | 247 |
| -6 | 6 | 350 | 363 |
| -7 | 6 | 257 | 255 |
| -8 | 6 | 226 | 223 |
| 0 | 7 | 489 | 492 |
| -1 | 7 | 448 | 428 |
| 1 | 7 | 617 | 624 |
| -2 | 7 | 506 | 504 |
| -3 | 7 | 40 | 14 |
| -4 | 7 | 272 | 264 |
| -5 | 7 | 105 | 78 |
| -6 | 7 | 524 | 543 |
| -7 | 7 | 433 | 447 |
| -1 | 8 | 60 | 29 |
| -2 | 8 | 64 | 52 |
| -3 | 8 | 86 | 73 |
| -4 | 8 | 381 | 376 |
| -5 | 8 | 528 | 522 |
| -6 | 8 | 317 | 318 |
| **K = 5**** | | | |
| 1 | 0 | 520 | 539 |
| 2 | 0 | 90 | 85 |
| 3 | 0 | 880 | 905 |
| 4 | 0 | 613 | 587 |
| 5 | 0 | 766 | 747 |
| 6 | 0 | 892 | 881 |
| 7 | 0 | 338 | 324 |
| 0 | 1 | 774 | 760 |
| 1 | 1 | 110 | 115 |
| -1 | 1 | 419 | 397 |
| -2 | 1 | 1228 | 1247 |
| 2 | 1 | 236 | 261 |
| -3 | 1 | 124 | 82 |
| 3 | 1 | 502 | 495 |
| -4 | 1 | 60 | 8 |
| 4 | 1 | 223 | 211 |
| 5 | 1 | 119 | 101 |
| -5 | 1 | 139 | 114 |
| 6 | 1 | 327 | 308 |
| -6 | 1 | 73 | 15 |
| -7 | 1 | 132 | 117 |
| 0 | 2 | 1422 | 1413 |
| -1 | 2 | 1561 | 1645 |
| 1 | 2 | 1201 | 1188 |
| 2 | 2 | 1437 | 1483 |
| -2 | 2 | 615 | 620 |
| -3 | 2 | 773 | 812 |
| 3 | 2 | 669 | 682 |
| -4 | 2 | 85 | 62 |
| 4 | 2 | 460 | 446 |
| -5 | 2 | 222 | 220 |
| 5 | 2 | 409 | 387 |
| -6 | 2 | 168 | 147 |
| 6 | 2 | 73 | 7 |
| -7 | 2 | 674 | 654 |
| -8 | 2 | 223 | 216 |
| 0 | 3 | 472 | 443 |
| -1 | 3 | 431 | 446 |
| 1 | 3 | 167 | 174 |
| -2 | 3 | 186 | 182 |
| 2 | 3 | 408 | 413 |
| 3 | 3 | 108 | 92 |
| -3 | 3 | 275 | 271 |
| 4 | 3 | 130 | 132 |
| -4 | 3 | 561 | 584 |
| -5 | 3 | 189 | 195 |
| 5 | 3 | 52 | 46 |
| -6 | 3 | 61 | 60 |
| -7 | 3 | 423 | 414 |
| -8 | 3 | 178 | 175 |
| -1 | 4 | 1103 | 1125 |
| 1 | 4 | 904 | 900 |
| -2 | 4 | 1063 | 1105 |
| 2 | 4 | 351 | 355 |
| -3 | 4 | 830 | 828 |
| 3 | 4 | 76 | 49 |
| 4 | 4 | 67 | 44 |
| -4 | 4 | 1109 | 1144 |
| -5 | 4 | 609 | 621 |
| -6 | 4 | 561 | 566 |
| -7 | 4 | 473 | 474 |
| -8 | 4 | 318 | 315 |
| 0 | 5 | 315 | 305 |
| -1 | 5 | 95 | 59 |
| 1 | 5 | 118 | 138 |
| -2 | 5 | 684 | 670 |
| 2 | 5 | 142 | 135 |
| -3 | 5 | 564 | 591 |
| 3 | 5 | 124 | 104 |
| -4 | 5 | 161 | 142 |
| -5 | 5 | 97 | 74 |
| -6 | 5 | 267 | 256 |
| -7 | 5 | 78 | 59 |
| -8 | 5 | 136 | 114 |
| 0 | 6 | 187 | 167 |
| -1 | 6 | 438 | 436 |
| 1 | 6 | 527 | 533 |
| -2 | 6 | 316 | 317 |
| 2 | 6 | 477 | 506 |
| -3 | 6 | 342 | 311 |
| -4 | 6 | 394 | 397 |
| -5 | 6 | 942 | 978 |
| -6 | 6 | 431 | 426 |
| -7 | 6 | 478 | 490 |
| -8 | 6 | 491 | 514 |
| 0 | 7 | 52 | 17 |
| -1 | 7 | 483 | 481 |
| 1 | 7 | 47 | 35 |
| -2 | 7 | 452 | 445 |
| -3 | 7 | 128 | 120 |
| -4 | 7 | 221 | 210 |
| -5 | 7 | 39 | 17 |
| -6 | 7 | 96 | 78 |
| -7 | 7 | 153 | 159 |
| -1 | 8 | 444 | 461 |
| -2 | 8 | 677 | 677 |
| -3 | 8 | 352 | 359 |
| -4 | 8 | 230 | 219 |
| -5 | 8 | 457 | 429 |
| -6 | 8 | 143 | 125 |
| **K = 6**** | | | |
| 0 | 0 | 12 | 39 |
| 1 | 0 | 255 | 259 |
| 2 | 0 | 411 | 416 |
| 3 | 0 | 152 | 162 |
| 4 | 0 | 335 | 325 |
| 5 | 0 | 143 | 144 |
| 6 | 0 | 236 | 237 |
| 7 | 0 | 319 | 324 |
| 0 | 1 | 717 | 729 |
| 1 | 1 | 901 | 906 |
| -1 | 1 | 752 | 801 |
| -2 | 1 | 86 | 59 |
| 2 | 1 | 1143 | 1182 |
| -3 | 1 | 158 | 137 |
| 3 | 1 | 1096 | 1094 |
| -4 | 1 | 892 | 900 |
| 4 | 1 | 659 | 632 |
| 5 | 1 | 787 | 796 |
| -5 | 1 | 553 | 532 |
| 6 | 1 | 461 | 466 |
| -6 | 1 | 749 | 732 |
| -7 | 1 | 581 | 591 |
| 0 | 2 | 217 | 216 |
| -1 | 2 | 176 | 207 |
| 1 | 2 | 56 | 37 |
| 2 | 2 | 509 | 484 |
| -2 | 2 | 397 | 386 |
| -3 | 2 | 749 | 776 |
| 3 | 2 | 873 | 891 |
| -4 | 2 | 567 | 580 |
| 4 | 2 | 225 | 216 |
| -5 | 2 | 49 | 9 |
| 5 | 2 | 154 | 123 |
| -6 | 2 | 143 | 125 |
| 6 | 2 | 189 | 170 |
| -7 | 2 | 186 | 182 |
| 0 | 3 | 528 | 492 |
| -1 | 3 | 1071 | 1130 |
| 1 | 3 | 451 | 429 |
| -2 | 3 | 856 | 870 |
| 2 | 3 | 639 | 616 |
| 3 | 3 | 298 | 298 |
| -3 | 3 | 934 | 991 |
| 4 | 3 | 184 | 199 |
| -4 | 3 | 588 | 607 |
| -5 | 3 | 237 | 224 |
| 5 | 3 | 114 | 120 |
| -6 | 3 | 226 | 207 |
| -7 | 3 | 230 | 232 |
| -8 | 3 | 594 | 600 |
| 0 | 4 | 178 | 164 |
| -1 | 4 | 81 | 79 |
| 1 | 4 | 81 | 65 |
| -2 | 4 | 535 | 559 |
| 2 | 4 | 259 | 251 |
| -3 | 4 | 139 | 145 |
| 3 | 4 | 276 | 273 |
| 4 | 4 | 507 | 559 |
| -4 | 4 | 145 | 131 |
| -5 | 4 | 197 | 196 |
| -6 | 4 | 197 | 204 |
| -7 | 4 | 897 | 890 |
| -8 | 4 | 444 | 436 |
| -1 | 5 | 623 | 619 |
| 1 | 5 | 178 | 187 |
| -2 | 5 | 888 | 904 |
| 2 | 5 | 566 | 575 |
| -3 | 5 | 356 | 360 |
| 3 | 5 | 239 | 243 |
| -4 | 5 | 751 | 745 |
| -5 | 5 | 850 | 855 |
| -6 | 5 | 524 | 531 |
| -7 | 5 | 591 | 589 |
| -8 | 5 | 302 | 264 |
| 0 | 6 | 77 | 63 |
| -1 | 6 | 135 | 123 |
| 1 | 6 | 62 | 35 |
| -2 | 6 | 178 | 154 |
| 2 | 6 | 276 | 273 |
| -3 | 6 | 77 | 65 |
| -4 | 6 | 404 | 392 |
| -5 | 6 | 161 | 162 |
| -6 | 6 | 569 | 582 |
| -7 | 6 | 77 | 29 |
| 0 | 7 | 246 | 241 |
| -1 | 7 | 223 | 214 |
| -2 | 7 | 531 | 516 |
| -3 | 7 | 123 | 113 |
| -4 | 7 | 57 | 57 |
| -5 | 7 | 527 | 530 |
| -6 | 7 | 521 | 544 |
| -7 | 7 | 420 | 407 |
| -2 | 8 | 183 | 179 |
| -3 | 8 | 268 | 266 |
| -4 | 8 | 67 | 41 |
| -5 | 8 | 67 | 42 |
| **K = 7**** | | | |
| 1 | 0 | 755 | 760 |
| 2 | 0 | 172 | 197 |
| 3 | 0 | 623 | 635 |
| 4 | 0 | 641 | 637 |
| 5 | 0 | 991 | 977 |
| 6 | 0 | 1116 | 1100 |
| 7 | 0 | 406 | 405 |
| 0 | 1 | 943 | 912 |
| 1 | 1 | 610 | 601 |
| -1 | 1 | 421 | 429 |
| -2 | 1 | 377 | 371 |
| 2 | 1 | 556 | 575 |
| -3 | 1 | 589 | 602 |
| 3 | 1 | 234 | 215 |
| -4 | 1 | 155 | 156 |
| 4 | 1 | 273 | 279 |
| 5 | 1 | 91 | 74 |
| -5 | 1 | 287 | 265 |
| 6 | 1 | 620 | 627 |
| -6 | 1 | 476 | 461 |
| -7 | 1 | 30 | 21 |
| 0 | 2 | 553 | 493 |
| -1 | 2 | 383 | 384 |
| 1 | 2 | 570 | 549 |
| 2 | 2 | 1005 | 1035 |
| -2 | 2 | 254 | 257 |
| -3 | 2 | 190 | 181 |
| 3 | 2 | 328 | 344 |
| -4 | 2 | 812 | 823 |
| 4 | 2 | 121 | 94 |
| -5 | 2 | 724 | 736 |
| 5 | 2 | 279 | 264 |
| -6 | 2 | 357 | 348 |
| -7 | 2 | 401 | 403 |
| 0 | 3 | 607 | 597 |
| -1 | 3 | 178 | 171 |
| 1 | 3 | 197 | 205 |
| -2 | 3 | 271 | 267 |
| 2 | 3 | 397 | 399 |
| 3 | 3 | 303 | 267 |
| -3 | 3 | 193 | 183 |
| 4 | 3 | 152 | 191 |
| -4 | 3 | 848 | 873 |
| -5 | 3 | 580 | 567 |
| 5 | 3 | 491 | 526 |
| -6 | 3 | 595 | 599 |
| -7 | 3 | 558 | 555 |
| 0 | 4 | 73 | 44 |
| -1 | 4 | 528 | 516 |
| 1 | 4 | 150 | 131 |
| -2 | 4 | 687 | 694 |
| 2 | 4 | 134 | 128 |
| -3 | 4 | 203 | 187 |
| 3 | 4 | 61 | 61 |
| 4 | 4 | 262 | 278 |
| -4 | 4 | 308 | 307 |
| -5 | 4 | 679 | 678 |
| -6 | 4 | 649 | 666 |
| -7 | 4 | 304 | 305 |
| 0 | 5 | 365 | 347 |
| -1 | 5 | 661 | 623 |
| 1 | 5 | 707 | 714 |
| -2 | 5 | 308 | 280 |
| 2 | 5 | 417 | 424 |
| -3 | 5 | 402 | 407 |
| 3 | 5 | 189 | 167 |
| -4 | 5 | 205 | 210 |
| -5 | 5 | 136 | 126 |
| -6 | 5 | 215 | 199 |
| -7 | 5 | 96 | 96 |
| 0 | 6 | 154 | 145 |
| -1 | 6 | 88 | 57 |
| 1 | 6 | 650 | 643 |
| -2 | 6 | 57 | 18 |
| 2 | 6 | 476 | 501 |
| -3 | 6 | 364 | 380 |
| -4 | 6 | 606 | 605 |
| -5 | 6 | 962 | 1019 |
| -6 | 6 | 781 | 816 |
| -7 | 6 | 377 | 386 |
| 0 | 7 | 246 | 226 |
| -1 | 7 | 37 | 16 |
| -2 | 7 | 275 | 266 |
| -3 | 7 | 487 | 474 |
| -4 | 7 | 357 | 351 |
| -5 | 7 | 581 | 566 |
| -6 | 7 | 395 | 391 |
| -3 | 8 | 117 | 125 |
| -4 | 8 | 230 | 226 |
| -5 | 8 | 54 | 10 |
| **K = 8**** | | | |
| 0 | 0 | 1349 | 1366 |
| 1 | 0 | 621 | 645 |
| 2 | 0 | 904 | 971 |
| 3 | 0 | 1184 | 1244 |
| 4 | 0 | 246 | 268 |
| 5 | 0 | 336 | 313 |
| 6 | 0 | 36 | 9 |
| 0 | 1 | 208 | 175 |
| 1 | 1 | 582 | 570 |
| -1 | 1 | 295 | 331 |
| -2 | 1 | 277 | 257 |
| 2 | 1 | 857 | 881 |
| -3 | 1 | 185 | 192 |
| 3 | 1 | 581 | 595 |
| -4 | 1 | 225 | 234 |
| 4 | 1 | 369 | 343 |
| 5 | 1 | 491 | 492 |
| -5 | 1 | 543 | 549 |
| -6 | 1 | 458 | 454 |
| -7 | 1 | 265 | 253 |
| 0 | 2 | 122 | [illegible] |
| -1 | 2 | 1303 | 1352 |
| 1 | 2 | 136 | 76 |
| 2 | 2 | 177 | 163 |
| -2 | 2 | 795 | 820 |
| -3 | 2 | 776 | 801 |
| 3 | 2 | 445 | 434 |
| -4 | 2 | 756 | 753 |
| 4 | 2 | 44 | 17 |
| -5 | 2 | 327 | 330 |
| 5 | 2 | 347 | 341 |
| -6 | 2 | 474 | 476 |
| -7 | 2 | 123 | 111 |
| 0 | 3 | 291 | 268 |
| -1 | 3 | 500 | 504 |
| 1 | 3 | 120 | 97 |
| -2 | 3 | 784 | 806 |
| 2 | 3 | 347 | 347 |
| 3 | 3 | 65 | 73 |
| -3 | 3 | 489 | 497 |
| 4 | 3 | 55 | 45 |
| -4 | 3 | 32 | 33 |
| -5 | 3 | 36 | 36 |
| -6 | 3 | 175 | 155 |
| -7 | 3 | 298 | 281 |
| 0 | 4 | 210 | 178 |
| -1 | 4 | 413 | 393 |
| 1 | 4 | 533 | 536 |
| -2 | 4 | 145 | 153 |
| 2 | 4 | 806 | 832 |
| -3 | 4 | 479 | 486 |
| 3 | 4 | 398 | 418 |
| 4 | 4 | 533 | 542 |
| -4 | 4 | 107 | 66 |
| -5 | 4 | 382 | 356 |
| -6 | 4 | 109 | 82 |
| -7 | 4 | 491 | 494 |
| 0 | 5 | 68 | 94 |
| -1 | 5 | 446 | 452 |
| 1 | 5 | 301 | 290 |
| -2 | 5 | 589 | 614 |
| 2 | 5 | 390 | 384 |
| -3 | 5 | 165 | 143 |
| 3 | 5 | 231 | 247 |
| -4 | 5 | 287 | 294 |
| -5 | 5 | 543 | 546 |
| -6 | 5 | 374 | 355 |
| -7 | 5 | 351 | 357 |
| 0 | 6 | 593 | 596 |
| -1 | 6 | 739 | 730 |
| 1 | 6 | 410 | 396 |
| -2 | 6 | 1071 | 1066 |
| -3 | 6 | 721 | 723 |
| -4 | 6 | 509 | 525 |
| -5 | 6 | 321 | 331 |
| -6 | 6 | 77 | 44 |
| -7 | 6 | 141 | 135 |
| 0 | 7 | 84 | 21 |
| -1 | 7 | 149 | 155 |
| -2 | 7 | 250 | 256 |
| -3 | 7 | 164 | 151 |
| -4 | 7 | 98 | 66 |
| -5 | 7 | 364 | 361 |
| -6 | 7 | 423 | 416 |
| **K = 9**** | | | |
| 1 | 0 | 76 | 53 |
| 2 | 0 | 64 | 49 |
| 3 | 0 | 248 | 254 |
| 4 | 0 | 188 | 186 |
| 5 | 0 | 311 | 311 |
| 6 | 0 | 246 | 224 |
| 0 | 1 | 1092 | 1074 |
| -1 | 1 | 1292 | 1327 |
| 1 | 1 | 723 | 720 |
| -2 | 1 | 942 | 990 |
| 2 | 1 | 979 | 1003 |
| -3 | 1 | 925 | 943 |
| 3 | 1 | 387 | 372 |
| -4 | 1 | 305 | 304 |
| 4 | 1 | 108 | 93 |
| 5 | 1 | 351 | 350 |
| -5 | 1 | 415 | 395 |
| -6 | 1 | 653 | 651 |
| 0 | 2 | 652 | 651 |
| -1 | 2 | 223 | 238 |
| 1 | 2 | 613 | 611 |
| 2 | 2 | 290 | 280 |
| -2 | 2 | 466 | 506 |
| -3 | 2 | 242 | 248 |
| 3 | 2 | 107 | 92 |
| -4 | 2 | 171 | 183 |
| 4 | 2 | 57 | 12 |
| -5 | 2 | 223 | 205 |
| 5 | 2 | 65 | 51 |
| -6 | 2 | 56 | 55 |
| -7 | 2 | 127 | 122 |
| 0 | 3 | 392 | 372 |
| -1 | 3 | 264 | 261 |
| 1 | 3 | 357 | 346 |
| -2 | 3 | 186 | 193 |
| 2 | 3 | 539 | 519 |
| 3 | 3 | 162 | 162 |
| -3 | 3 | 227 | 201 |
| 4 | 3 | 275 | 282 |
| -4 | 3 | 882 | 883 |
| -5 | 3 | 753 | 761 |
| -6 | 3 | 531 | 524 |
| -7 | 3 | 490 | 524 |
| 0 | 4 | 212 | 208 |
| -1 | 4 | 334 | 332 |
| 1 | 4 | 196 | 196 |
| -2 | 4 | 210 | 206 |
| 2 | 4 | 259 | 262 |
| -3 | 4 | 60 | 19 |
| 3 | 4 | 285 | 268 |
| -4 | 4 | 270 | 287 |
| -5 | 4 | 325 | 317 |
| -6 | 4 | 328 | 325 |
| -7 | 4 | 143 | 127 |
| 0 | 5 | 563 | 555 |
| -1 | 5 | 972 | 974 |
| -1 | 5 | 972 | 974 |
| 1 | 5 | 952 | 953 |
| -2 | 5 | 705 | 711 |
| 2 | 5 | 772 | 778 |
| -3 | 5 | 390 | 401 |
| -4 | 5 | 321 | 311 |
| -5 | 5 | 310 | 317 |
| -6 | 5 | 189 | 184 |
| -7 | 5 | 107 | 82 |
| 0 | 6 | 209 | 202 |
| -1 | 6 | 56 | 44 |
| 1 | 6 | 241 | 232 |
| -2 | 6 | 178 | 126 |
| -3 | 6 | 69 | 91 |
| -4 | 6 | 274 | 254 |
| -5 | 6 | 272 | 271 |
| -6 | 6 | 154 | 160 |
| -1 | 7 | 370 | 391 |
| -2 | 7 | 746 | 730 |
| -3 | 7 | 519 | 499 |
| -4 | 7 | 481 | 498 |
| -5 | 7 | 832 | 870 |
| **K = 10**** | | | |
| 0 | 0 | 749 | 722 |
| 1 | 0 | 501 | 486 |
| 2 | 0 | 1055 | 1125 |
| 3 | 0 | 782 | 797 |
| 4 | 0 | 50 | 78 |
| 5 | 0 | 272 | 248 |
| 6 | 0 | 77 | 66 |
| 0 | 1 | 142 | 83 |
| 1 | 1 | 97 | 123 |
| -1 | 1 | 29 | 11 |
| -2 | 1 | 45 | 14 |
| 2 | 1 | 17 | 18 |
| -3 | 1 | 234 | 237 |
| 3 | 1 | 242 | 231 |
| -4 | 1 | 450 | 442 |
| 4 | 1 | 144 | 136 |
| 5 | 1 | 195 | 190 |
| -5 | 1 | 259 | 248 |
| -6 | 1 | 364 | 375 |
| 0 | 2 | 25 | 23 |
| -1 | 2 | 1025 | 1069 |
| 1 | 2 | 166 | 111 |
| 2 | 2 | 232 | 213 |
| -2 | 2 | 938 | 976 |
| -3 | 2 | 614 | 636 |
| 3 | 2 | 414 | 401 |
| -4 | 2 | 743 | 749 |
| 4 | 2 | 272 | 260 |
| -5 | 2 | 550 | 537 |
| 5 | 2 | 644 | 607 |
| -6 | 2 | 733 | 747 |
| 0 | 3 | 157 | 151 |
| -1 | 3 | 127 | 118 |
| 1 | 3 | 72 | 68 |
| -2 | 3 | 451 | 455 |
| 2 | 3 | 59 | 11 |
| 3 | 3 | 139 | 122 |
| -3 | 3 | 373 | 365 |
| 4 | 3 | 165 | 128 |
| -4 | 3 | 233 | 256 |
| -5 | 3 | 332 | 355 |
| -6 | 3 | 158 | 138 |
| -7 | 3 | 112 | 95 |
| 0 | 4 | 156 | 135 |
| -1 | 4 | 322 | 318 |
| 1 | 4 | 559 | 559 |
| -2 | 4 | 151 | 146 |
| 2 | 4 | 960 | 989 |
| -3 | 4 | 178 | 169 |
| 3 | 4 | 467 | 470 |
| -4 | 4 | 180 | 147 |
| -5 | 4 | 652 | 651 |
| -6 | 4 | 436 | 449 |
| -7 | 4 | 504 | 511 |
| 0 | 5 | 276 | 273 |
| -1 | 5 | 267 | 254 |
| -1 | 5 | 267 | 254 |
| 1 | 5 | 49 | 66 |
| -2 | 5 | 60 | 71 |
| 2 | 5 | 118 | 101 |
| -3 | 5 | 222 | 205 |
| -4 | 5 | 134 | 134 |
| -5 | 5 | 315 | 328 |
| -6 | 5 | 164 | 172 |
| 0 | 6 | 327 | 319 |
| -1 | 6 | 682 | 647 |
| -2 | 6 | 1088 | 1094 |
| -3 | 6 | 458 | 455 |
| -4 | 6 | 285 | 289 |
| -5 | 6 | 261 | 290 |
| -6 | 6 | 107 | 108 |
| -2 | 7 | 112 | 121 |
| -3 | 7 | 374 | 393 |
| -4 | 7 | 218 | 220 |
| **K = 11**** | | | |
| 1 | 0 | 763 | 795 |
| 2 | 0 | 117 | 118 |
| 3 | 0 | 294 | 289 |
| 4 | 0 | 294 | 315 |
| 5 | 0 | 173 | 149 |
| 0 | 1 | 419 | 388 |
| 1 | 1 | 85 | 43 |
| -1 | 1 | 848 | 856 |
| -2 | 1 | 454 | 447 |
| 2 | 1 | 469 | 485 |
| -3 | 1 | 608 | 612 |
| 3 | 1 | 150 | 155 |
| -4 | 1 | 223 | 215 |
| 4 | 1 | 459 | 460 |
| 5 | 1 | 477 | 470 |
| -5 | 1 | 408 | 384 |
| -6 | 1 | 459 | 456 |
| -5 | 1 | 408 | 364 |
| 0 | 2 | 42 | 3 |
| -1 | 2 | 141 | 161 |
| 1 | 2 | 160 | 185 |
| 2 | 2 | 481 | 480 |
| -2 | 2 | 58 | 48 |
| -3 | 2 | 430 | 439 |
| 3 | 2 | 335 | 330 |
| -4 | 2 | 115 | 96 |
| 4 | 2 | 72 | 49 |
| -5 | 2 | 168 | 201 |
| -6 | 2 | 78 | 32 |
| 0 | 3 | 291 | 248 |
| -1 | 3 | 95 | 95 |
| 1 | 3 | 396 | 368 |
| -2 | 3 | 338 | 341 |
| 2 | 3 | 574 | 564 |
| 3 | 3 | 447 | 464 |
| -3 | 3 | 335 | 343 |
| -4 | 3 | 761 | 774 |
| -5 | 3 | 939 | 963 |
| -6 | 3 | 787 | 790 |
| 0 | 4 | 86 | 70 |
| -1 | 4 | 409 | 401 |
| 1 | 4 | 58 | 72 |
| -2 | 4 | 510 | 508 |
| 2 | 4 | 192 | 196 |
| -3 | 4 | 178 | 191 |
| -4 | 4 | 201 | 197 |
| -6 | 4 | 124 | 120 |
| 0 | 5 | 369 | 348 |
| -1 | 5 | 420 | 411 |
| -1 | 5 | 420 | 411 |
| 1 | 5 | 609 | 607 |
| -2 | 5 | 349 | 345 |
| -3 | 5 | 79 | 55 |
| -4 | 5 | 231 | 226 |
| -5 | 5 | 343 | 321 |
| -6 | 5 | 170 | 201 |
| 0 | 6 | 245 | 225 |
| -1 | 6 | 265 | 257 |
| -2 | 6 | 92 | 69 |
| -3 | 6 | 56 | 24 |
| -4 | 6 | 39 | 19 |
| -5 | 6 | 374 | 365 |
| **K = 12**** | | | |
| 0 | 0 | 327 | 315 |
| 1 | 0 | 331 | 324 |
| 2 | 0 | 363 | 364 |
| 3 | 0 | 227 | 222 |
| 4 | 0 | 116 | 129 |
| 5 | 0 | 79 | 45 |
| 0 | 1 | 477 | 474 |
| 1 | 1 | 531 | 518 |
| -1 | 1 | 97 | 56 |
| -2 | 1 | 491 | 469 |
| 2 | 1 | 388 | 379 |
| -3 | 1 | 229 | 207 |
| 3 | 1 | 312 | 304 |
| -4 | 1 | 384 | 359 |
| 4 | 1 | 115 | 95 |
| -5 | 1 | 341 | 327 |
| 0 | 2 | 155 | 158 |
| -1 | 2 | 462 | 471 |
| 1 | 2 | 236 | 210 |
| 2 | 2 | 388 | 377 |
| -2 | 2 | 445 | 424 |
| -3 | 2 | 596 | 591 |
| 3 | 2 | 277 | 285 |
| -4 | 2 | 712 | 725 |
| 4 | 2 | 456 | 452 |
| -5 | 2 | 382 | 383 |
| -6 | 2 | 444 | 446 |
| 0 | 3 | 448 | 409 |
| -1 | 3 | 815 | 832 |
| 1 | 3 | 576 | 540 |
| -2 | 3 | 415 | 425 |
| 2 | 3 | 764 | 782 |
| 3 | 3 | 179 | 175 |
| -3 | 3 | 409 | 405 |
| -4 | 3 | 38 | 58 |
| -5 | 3 | 56 | 19 |
| -6 | 3 | 441 | 430 |
| 0 | 4 | 301 | 289 |
| -1 | 4 | 86 | 86 |
| 1 | 4 | 352 | 334 |
| -2 | 4 | 150 | 147 |
| 2 | 4 | 443 | 444 |
| -3 | 4 | 55 | 21 |
| -4 | 4 | 290 | 305 |
| -5 | 4 | 542 | 559 |
| -6 | 4 | 351 | 348 |
| 0 | 5 | 97 | 76 |
| -1 | 5 | 160 | 140 |
| 1 | 5 | 73 | 16 |
| -2 | 5 | 413 | 409 |
| -3 | 5 | 69 | 75 |
| -4 | 5 | 342 | 352 |
| -5 | 5 | 709 | 729 |
| -1 | 6 | 348 | 347 |
| -2 | 6 | 445 | 450 |
| -3 | 6 | 277 | 269 |
| -4 | 6 | 285 | 313 |
| **K = 13**** | | | |
| 1 | 0 | 437 | 411 |
| 2 | 0 | 383 | 406 |
| 3 | 0 | 358 | 359 |
| 4 | 0 | 208 | 214 |
| 0 | 1 | 513 | 507 |
| 1 | 1 | 423 | 376 |
| -1 | 1 | 406 | 414 |
| -2 | 1 | 287 | 293 |
| 2 | 1 | 189 | 196 |
| -3 | 1 | 312 | 291 |
| 3 | 1 | 49 | 17 |
| -4 | 1 | 432 | 417 |
| 4 | 1 | 146 | 121 |
| -5 | 1 | 260 | 249 |
| 0 | 2 | 447 | 410 |
| -1 | 2 | 475 | 491 |
| 1 | 2 | 481 | 485 |
| 2 | 2 | 940 | 957 |
| -2 | 2 | 579 | 603 |
| -3 | 2 | 677 | 692 |
| 3 | 2 | 502 | 503 |
| -4 | 2 | 128 | 106 |
| -5 | 2 | 163 | 73 |
| 0 | 3 | 142 | 113 |
| -1 | 3 | 221 | 222 |
| 1 | 3 | 62 | 15 |
| -2 | 3 | 124 | 117 |
| 2 | 3 | 217 | 227 |
| -3 | 3 | 356 | 372 |
| -4 | 3 | 270 | 286 |
| -5 | 3 | 257 | 251 |
| 0 | 4 | 231 | 200 |
| -1 | 4 | 902 | 895 |
| 1 | 4 | 367 | 360 |
| -2 | 4 | 996 | 1023 |
| -3 | 4 | 434 | 454 |
| -4 | 4 | 583 | 595 |
| -5 | 4 | 210 | 229 |
| 0 | 5 | 450 | 436 |
| -1 | 5 | 318 | 294 |
| -2 | 5 | 223 | 232 |
| -3 | 5 | 124 | 104 |
| -4 | 5 | 121 | 129 |
| **K = 14**** | | | |
| 0 | 0 | 395 | 402 |
| 1 | 0 | 448 | 455 |
| 2 | 0 | 214 | 223 |
| 3 | 0 | 142 | 151 |
| 4 | 0 | 350 | 337 |
| 0 | 1 | 715 | 716 |
| 1 | 1 | 486 | 464 |
| -1 | 1 | 107 | 102 |
| -2 | 1 | 257 | 238 |
| 2 | 1 | 365 | 346 |
| -3 | 1 | 110 | 81 |
| 3 | 1 | 551 | 551 |
| -4 | 1 | 528 | 538 |
| 0 | 2 | 300 | 276 |
| -1 | 2 | 70 | 13 |
| 1 | 2 | 227 | 227 |
| 2 | 2 | 71 | 53 |
| -2 | 2 | 115 | 118 |
| -3 | 2 | 383 | 393 |
| 3 | 2 | 106 | 113 |
| -4 | 2 | 151 | 148 |
| 0 | 3 | 602 | 575 |
| -1 | 3 | 768 | 820 |
| 1 | 3 | 680 | 666 |
| -2 | 3 | 444 | 437 |
| 2 | 3 | 651 | 643 |
| -3 | 3 | 368 | 348 |
| -4 | 3 | 227 | 233 |
| 0 | 4 | 280 | 278 |
| -1 | 4 | 292 | 281 |
| -2 | 4 | 120 | 112 |
| -3 | 4 | 39 | 30 |
| -4 | 4 | 223 | 236 |
| -2 | 5 | 356 | 340 |
| -3 | 5 | 344 | 333 |
| **K = 15**** | | | |
| 1 | 0 | 358 | 352 |
| 2 | 0 | 334 | 352 |
| 3 | 0 | 689 | 760 |
| 0 | 1 | 252 | 230 |
| 1 | 1 | 358 | 335 |
| -1 | 1 | 77 | 58 |
| -2 | 1 | 40 | 14 |
| 2 | 1 | 183 | 155 |
| -3 | 1 | 83 | 75 |
| 3 | 1 | 86 | 74 |
| 0 | 2 | 430 | 410 |
| -1 | 2 | 198 | 193 |
| 1 | 2 | 302 | 315 |
| 2 | 2 | 441 | 464 |
| -2 | 2 | 67 | 58 |
| -3 | 2 | 241 | 248 |
| -4 | 2 | 88 | 92 |
| 0 | 3 | 20 | 6 |
| -1 | 3 | 219 | 197 |
| 1 | 3 | 71 | 28 |
| -2 | 3 | 176 | 151 |
| -3 | 3 | 144 | 121 |
| -1 | 4 | 509 | 498 |
| -2 | 4 | 522 | 517 |
| **K = 16**** | | | |
| 0 | 0 | 257 | 241 |
| 1 | 0 | 188 | 171 |
| 2 | 0 | 338 | 347 |
| 0 | 1 | 428 | 408 |
| 1 | 1 | 172 | 166 |
| -1 | 1 | 305 | 311 |
| -2 | 1 | 119 | 116 |
| 0 | 2 | 19 | 20 |
| -1 | 2 | 316 | 332 |
| 1 | 2 | 19 | 20 |
| -2 | 2 | 132 | 143 |

computer provided by P. F. Stokely. Reflections were placed on an absolute scale by a Wilson plot and normalized structure factors ($E$'s) were computed. The 400 largest $E$'s were employed in the MAGIC program, and 386 signs were determined using the criterion that the ratio of consistencies to inconsistencies for the sign must exceed 5.

An $E$ map was prepared using the 386 signed reflections of the most probable set. One Mo atom on a fourfold (general) position and four Cl atoms, also in general positions, were clearly revealed. No lighter atoms were distinct. Two cycles of least-squares refinement of the positional and isotropic thermal parameters of these five atoms as well as the over-all scale factor were carried out, where the value of $R_1 = (\Sigma||F_o| - |F_c||)/|F_o|$ was 0.175. A difference Fourier synthesis now indicated the positions of the lighter atoms (two C's, two N's, and one O) all in general positions. Three more cycles of isotropic refinement of all atoms brought $R_1$ to 0.096. The absorption corrections were now applied, and after three more cycles of isotropic refinement of unit-weighted data, convergence was reached with $R_1 = 0.075$.

In these and subsequent stages of refinement, structure factors for neutral Mo, Cl, C, N, and O atoms were taken from Cromer and Waber.[13] Scattering factors for hydrogen atoms were those of Mason and Robertson.[14] For Mo and Cl the structure factors were corrected for the real and imaginary components of anomalous scattering.[15]

Refinement was continued using weighted data and anisotropic temperature parameters. The weighting factor, $w$, for a reflection was taken as $[\sigma(F)]^{-2}$ where $\sigma(F)$ is the standard deviation of the observed structure factor, as defined in the Experimental Section. The weighted residual, $R_2$, is given by the expression $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Anisotropic temperature factors were expressed in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Two cycles of anisotropic refinement led to the residuals $R_1 = 0.050$ and $R_2 = 0.071$.

It was observed that for 32 reflections which originally had peak counts exceeding 10,000 extinction effects were apparently appreciable. Therefore corrections of the form recommended by Zachariasen[16] were applied. In the equation $F_c \approx KF_o(1 + B_{2\theta}CP)$, where $P$ represents the peak count and $C$ and $K$ are scale factors, $B_{2\theta}$ was also treated as a constant independent of $2\theta$. Two cycles of refinement including

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[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

[14] R. Mason and G. B. Robertson in "Advances in Structural Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 57.

[15] D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

[16] W. H. Zachariasen, *ibid.*, **16**, 1139 (1963).

the secondary extinction corrections resulted in $R_1$ = 0.047 and $R_2$ = 0.069.

A difference electron density map now showed the positions of 12 hydrogen atoms, which were included in two further cycles of least-squares refinement, which led to the residuals $R_1$ = 0.040 and $R_2$ = 0.055. The H atom positions are undoubtedly rather inaccurate because of the dominance of the heavy-atom scattering, errors in the absorption corrections, and neglect of multiple scattering effects. Agreement between $F_o$ and $F_c$ for the 402 reflection is singularly poor, presumably due to some large error in $F_o$. The standard deviation of an observation of unit weight is 1.04 and in the final cycle of refinement no positional parameter changed by more than half of its standard deviation. A final difference electron density map had no peak larger than about 0.5 e$^-$ Å$^{-3}$. A list of the observed and final calculated structure factors is given in Table I.

## Results

The positional coordinates of all atoms are listed in Table II, along with their isotropic thermal vibration parameters, or equivalent values derived from the tensors of anisotropic vibration. The components of the anisotropic temperature parameter tensors for Mo, Cl, N, C, and O atoms are given in Table III. Rms amplitudes of vibration and their direction cosines are listed in Table IV.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS[a]

| Atom | x | y | z | B,[b] Å$^2$ |
|---|---|---|---|---|
| Mo | 0.54675 (8) | 0.44965 (4) | 0.09356 (8) | 1.34 |
| Cl(1) | 0.88168 (26) | 0.44193 (13) | 0.20193 (28) | 2.49 |
| Cl(2) | 0.53013 (28) | 0.32450 (13) | 0.91913 (28) | 2.49 |
| Cl(3) | 0.26838 (26) | 0.39710 (13) | 0.09745 (27) | 2.36 |
| Cl(4) | 0.62606 (27) | 0.51537 (14) | 0.38046 (25) | 2.39 |
| O | 0.2002 (9) | 0.2937 (4) | 0.4083 (10) | 2.90 |
| N(1) | 0.9229 (12) | 0.6408 (8) | 0.3570 (13) | 2.68 |
| N(2) | 0.1998 (13) | 0.5791 (6) | 0.2280 (13) | 3.27 |
| C(1) | 0.1076 (13) | 0.6737 (6) | 0.4074 (13) | 2.46 |
| C(2) | 0.1643 (14) | 0.6654 (6) | 0.2630 (13) | 2.50 |
| H(1O) | 0.267 (17) | 0.312 (8) | 0.353 (16) | 6.5 (3.2) |
| H(2O) | 0.306 (13) | 0.275 (6) | 0.486 (12) | 2.6 (1.9) |
| H(1N1) | 0.878 (10) | 0.648 (5) | 0.465 (11) | 2.9 (1.5) |
| H(2N1) | 0.847 (13) | 0.652 (6) | 0.248 (13) | 7.5 (1.9) |
| H(3N1) | 0.891 (14) | 0.602 (7) | 0.313 (14) | 6.7 (2.4) |
| H(1N2) | 0.181 (12) | 0.649 (5) | 0.497 (13) | 2.4 (1.8) |
| H(2N2) | 0.052 (12) | 0.696 (6) | 0.143 (12) | 3.9 (1.8) |
| H(3N2) | 0.260 (11) | 0.704 (5) | 0.288 (10) | 2.6 (1.5) |
| H(1C1) | 0.098 (16) | 0.558 (7) | 0.181 (14) | 4.5 (2.4) |
| H(2C1) | 0.111 (12) | 0.735 (6) | 0.447 (12) | 4.6 (1.9) |
| H(1C2) | 0.252 (16) | 0.591 (8) | 0.174 (16) | 4.8 (2.9) |
| H(2C2) | 0.202 (15) | 0.543 (7) | 0.291 (15) | 4.3 (2.6) |

[a] Standard deviations occurring in the last significant figure are given in parentheses. [b] B's without standard deviations are those calculated from the anisotropic tensors of Table III.

The $Mo_2Cl_8^{4-}$ ion is depicted in Figure 1, which also shows the numbering scheme. Atoms denoted with primes are related to unprimed atoms with the same number by the crystallographic center of symmetry which lies between the two Mo atoms. Table V gives the interatomic distances and bond angles of the $Mo_2Cl_8^{4-}$ ion. The important interatomic distances and bond angles of the ethylenediammonium ion and the $H_2O$ molecule are collected in Table VI. Intermolecular contacts less than 4 Å are listed in Table VII.

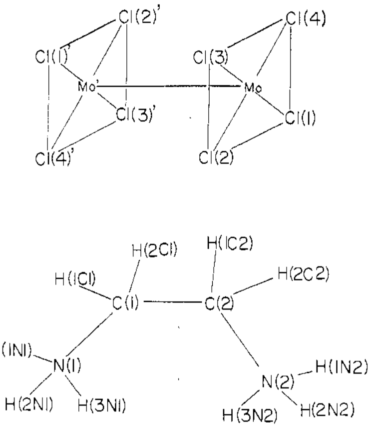

Figure 1.—Sketch of the $Mo_2Cl_8^{4-}$ and $NH_3CH_2CH_3NH_3^{2+}$ ions showing the numbering scheme used in the tables.

TABLE III

ANISOTROPIC TEMPERATURE PARAMETERS[a]

(Mo, ×10$^5$; OTHERS, ×10$^4$)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Mo | 529 (16) | 168 (15) | 598 (15) | 22 (4) | 324 (11) | 46 (4) |
| Cl(1) | 70 (4) | 32 (1) | 120 (4) | 6 (2) | 44 (3) | 8 (2) |
| Cl(2) | 132 (4) | 19 (1) | 145 (4) | −5 (2) | 87 (4) | 5 (2) |
| Cl(3) | 107 (4) | 26 (1) | 120 (4) | −12 (2) | 77 (3) | −2 (2) |
| Cl(4) | 117 (4) | 32 (1) | 73 (4) | 4 (4) | 53 (3) | 3 (2) |
| O | 144 (15) | 24 (3) | 159 (14) | 9 (6) | 87 (14) | 1 (5) |
| N(1) | 130 (18) | 44 (5) | 118 (18) | 7 (8) | 61 (15) | 7 (8) |
| N(2) | 126 (20) | 29 (4) | 148 (18) | 5 (8) | 98 (16) | −3 (8) |
| C(1) | 138 (21) | 24 (5) | 100 (19) | 7 (8) | 64 (17) | 8 (8) |
| C(2) | 167 (21) | 16 (4) | 146 (20) | 8 (8) | 109 (17) | 2 (7) |

[a] Standard deviations occurring in the last quoted figure are given in parentheses.

## Discussion

The substance studied here has the formula $(H_3NCH_2CH_2NH_3)_2Mo_2Cl_8 \cdot 2H_2O$ according to elemental analyses and the complete solution of the crystal structure by X-ray diffraction. Comparison of both analytical data and X-ray data shows that the microscopically crystalline material initially obtained from the preparative reaction and the larger crystals obtained by recrystallization are chemically identical.

The compound contains the $Mo_2Cl_8^{4-}$ ion which we previously discovered[3] in $K_4Mo_2Cl_8 \cdot 2H_2O$. The dimensions found here for $Mo_2Cl_8^{4-}$ do not differ significantly from those observed in $K_4Mo_2Cl_8 \cdot 2H_2O$ but they are more accurate. The Mo–Mo distance here is 2.134 (1) Å while that obtained from the study of $K_4Mo_2Cl_8 \cdot 2H_2O$ was nominally 2.139 (4) Å with the actual uncertainty being presumably larger than 0.004 Å because of a disordering of the pairs of Mo atoms in the $Cl_8$ cubes. As stated and discussed before,[3] this Mo–Mo distance is indicative of very strong Mo–Mo

TABLE IV
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION AND THEIR DIRECTION COSINES[a]

| Atom | Minor axis | Medium axis | Major axis |
|---|---|---|---|
| Mo | 0.109<br>(0.968, 0.074, −0.240) | 0.126<br>(0.249, −0.419, 0.873) | 0.152<br>(0.036, 0.905, 0.424) |
| Cl(1) | 0.133<br>(0.948, −0.105, 0.301) | 0.182<br>(−0.314, −0.461, 0.830) | 0.209<br>(−0.052, 0.881, 0.469) |
| Cl(2) | 0.142<br>(0.593, 0.765, −0.252) | 0.177<br>(0.753, −0.638, −0.161) | 0.208<br>(0.284, 0.095, 0.954) |
| Cl(3) | 0.129<br>(0.902, 0.339, −0.267) | 0.181<br>(−0.021, 0.652, 0.758) | 0.200<br>(−0.431, 0.678, −0.595) |
| Cl(4) | 0.134<br>(−0.446, −0.036, 0.894) | 0.175<br>(0.876, −0.221, 0.428) | 0.205<br>(0.182, 0.975, 0.130) |
| O | 0.164<br>(−0.667, 0.741, 0.077) | 0.192<br>(0.691, 0.655, −0.304) | 0.215<br>(0.276, 0.150, 0.949) |
| N(1) | 0.181<br>(−0.420, −0.133, 0.898) | 0.195<br>(0.227, 0.971, −0.078) | 0.212<br>(0.335, −0.003, 0.942) |
| N(2) | 0.137<br>(0.914, −0.240, −0.326) | 0.184<br>(0.903, −0.155, 0.400) | 0.240<br>(0.086, 0.979, 0.185) |
| C(1) | 0.154<br>(−0.282, −0.492, 0.824) | 0.174<br>(−0.655, 0.726, 0.209) | 0.198<br>(0.701, 0.481, 0.527) |
| C(20) | 0.135<br>(−0.455, 0.869, 0.194) | 0.163<br>(0.674, 0.479, −0.562) | 0.224<br>(0.582, 0.125, 0.804) |

[a] Direction cosines are referred to the orthogonal coordinate system *a*, *b*, *c**.

TABLE V
DIMENSIONS OF THE $Mo_2Cl_8^{4-}$ ION

| | |
|---|---|
| **A. Bond Lengths, Å** | |
| Mo–Mo′ | 2.134 (1) |
| Mo–Cl(1) | 2.460 (2) |
| Mo–Cl(2) | 2.453 (2) |
| Mo–Cl(3) | 2.451 (2) |
| Mo–Cl(4) | 2.442 (2) |
| Mo–Cl (mean) | 2.451 ± 0.005 |
| **B. Bond Angles, Deg** | |
| Cl(1)–Mo–Cl(2) | 85.41 (7) |
| Cl(2)–Mo–Cl(3) | 86.58 (7) |
| Cl(3)–Mo–Cl(4) | 87.01 (7) |
| Cl(4)–Mo–Cl(1) | 85.49 (7) |
| Cl(1)–Mo–Cl(3) | 149.82 (7) |
| Cl(2)–Mo–Cl(4) | 149.90 (7) |
| Cl–Mo–Cl (mean) | 86.1 ± 0.7 |
| | 149.86 ± 0.06 |
| Mo′–Mo–Cl(1) | 105.32 (6) |
| Mo′–Mo–Cl(2) | 105.48 (6) |
| Mo′–Mo–Cl(3) | 104.87 (6) |
| Mo′–Mo–Cl(4) | 104.58 (6) |
| Mo–Mo–Cl (mean) | 105.1 ± 0.4 |
| **C. Cl···Cl Contacts, Å** | |
| Cl(1)···Cl(2) | 3.332 (3) |
| Cl(2)····Cl(3) | 3.364 (3) |
| Cl(3)···Cl(4) | 3.367 (3) |
| Cl(4)···Cl(1) | 3.327 (3) |
| Cl···Cl (mean) | 3.35 ± 0.02 |
| **D. Cl···Cl′ Contacts, Å** | |
| Cl(1)···Cl(3)′ | 3.412 (3) |
| Cl(2)···Cl(4)′ | 3.404 (3) |
| Cl···Cl′ (mean) | 3.41 ± 0.01 |
| **E. Cl–Cl–Cl Angles, Deg** | |
| Cl(1)–Cl(2)–Cl(3) | 90.08 (7) |
| Cl(2)–Cl(3)–Cl(4) | 89.41 (7) |
| Cl(3)–Cl(4)–Cl(1) | 90.06 (7) |
| Cl(4)–Cl(1)–Cl(2) | 90.44 (7) |
| Cl–Cl–Cl (mean) | 90.0 ± 0.3 |
| **F. Cl–Cl–Cl′ Angles, Deg** | |
| Cl(1)–Cl(4)–Cl(2)′ | 91.26 (7) |
| Cl(2)–Cl(1)–Cl(3)′ | 90.03 (7) |
| Cl(3)–Cl(4)–Cl(2)′ | 89.59 (7) |
| Cl(4)–Cl(1)–Cl(3)′ | 89.36 (7) |
| Cl–Cl–Cl′ (mean) | 90.1 ± 0.8 |

TABLE VI
DIMENSIONS OF THE ETHYLENEDIAMMONIUM ION AND THE WATER MOLECULE[a]

| Distance | Value, Å | Bond angle | Value, deg |
|---|---|---|---|
| N(1)–C(1) | 1.466 (14) | N(1)–C(1)–C(2) | 113.9 (9) |
| N(2)–C(2) | 1.469 (14) | N(2)–C(2)–C(1) | 114.4 (8) |
| C(1)–C(2) | 1.507 (14) | C(1)–N(1)–H(1N1) | 114 (4) |
| N(1)–H(1N1) | 1.14 (8) | C(1)–N(1)–H(2N1) | 112 (6) |
| N(1)–H(2N1) | 0.86 (10) | C(1)–N(1)–H(3N1) | 123 (8) |
| N(1)–H(3N1) | 0.71 (11) | C(2)–N(2)–H(1N2) | 96 (9) |
| C(1)–H(1C1) | 1.03 (10) | C(2)–N(2)–H(2N2) | 120 (8) |
| C(1)–H(2C1) | 0.82 (10) | C(2)–N(2)–H(3N2) | 103 (7) |
| C(2)–H(1C2) | 1.11 (9) | H(1C1)–C(1)–H(2C1) | 105 (8) |
| C(2)–H(2C2) | 0.94 (8) | H(1C2)–C(2)–H(2C2) | 100 (7) |
| N(2)–H(1N2) | 0.79 (12) | H(1O)–O–H(2O) | 83 (10) |
| N(2)–H(2N2) | 0.78 (11) | | |
| N(2)–H(3N2) | 0.81 (12) | | |
| O–H(1O) | 0.92 (12) | | |
| O–H(2O) | 0.86 (9) | | |

[a] Standard deviations occurring in the least significant figure of each dimension are given in parentheses.

TABLE VII
NONBONDED INTERMOLECULAR CONTACTS (Å) LESS THAN 4 Å

| | | | |
|---|---|---|---|
| Cl(1) | to: | O $(1 + x, y, z)$ | 3.348 |
| | | N(1) $(x, y, z)$ | 3.394 |
| | | N(2) $(1 + x, y, z)$ | 3.337 |
| | | N(2) $(1 - x, 1 - y, -z)$ | 3.402 |
| Cl(2) | to: | O $(x, y, z)$ | 3.914 |
| | | O $(x, \frac{3}{2} - y, \frac{3}{2} + z)$ | 3.269 |
| | | N(1) $(1 - x, 1 - y, 1 - z)$ | 3.382 |
| | | N(2) $(1 - x, 1 - y, 1 - z)$ | 3.385 |
| Cl(3) | to: | O $(x, y, z)$ | 3.375 |
| | | O $(x, -\frac{3}{2} + y, \frac{1}{2} + z)$ | 3.367 |
| | | N(1) $(1 - x, 1 - y, -z)$ | 3.465 |
| | | N(2) $(x, y, z)$ | 3.254 |
| | | N(2) $(-x, 1 - y, -z)$ | 3.544 |
| Cl(4) | to: | O $(1 - x, 1 - y, 1 - z)$ | 3.485 |
| | | N(1) $(x, y, z)$ | 3.234 |
| | | N(2) $(x, y, z)$ | 3.272 |
| | | N(2) $(1 - x, 1 - y, 1 - z)$ | 3.298 |
| O | to: | N(1) $(1 - x, 1 - y, 1 - z)$ | 2.825 |
| | | N(1) $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ | 3.149 |
| N(1) | to: | N(2) $(1 + x, y, z)$ | 3.112 |

bonding. When compared with distances of ~2.6 and ~2.5 Å for single and double bonds, it suggests the presence of a triple or quadruple bond.

The rotational configuration of the $Mo_2Cl_8^{4-}$ ion is again found to be eclipsed (crystallographic symmetry $C_i$; virtual symmetry $D_{4h}$), which requires the presence of a significant $\delta$ component in the Mo–Mo bond and thus shows that this bond is quadruple.

In this compound the $Mo_2Cl_8^{4-}$ ion has a very regular square parallelepiped structure, which comes very close to containing a cubic array of eight Cl atoms. The bases of the parallelepiped formed by the sets of Cl atoms bound to each of the Mo atoms are square within the chemical significance of the data. The edges all lie within the range 3.332–3.367 Å and the Cl–Cl–Cl angles run from 89.4 to 90.4°. The vertical edges of the parallelepipid are 3.41 ± 0.01 Å. These vertical edges are longer than the eight basal edges by 0.06 Å, an amount which is highly significant statistically and undoubtedly this difference is real. Still, the difference is small both relatively (<2%) and in relation to the probable amplitudes of vibration for the Cl atoms, and thus the array of eight Cl atoms is scarcely different from cubic.

It may be noted that there is still no firm evidence that the treatment of $Mo_2(O_2CCH_3)_4$ with mineral acids produces other than dinuclear products.

The dimensions of the $H_3NCH_2CH_2NH_3^{2+}$ ion are normal and require no particular comment. It is interesting to note that the $H_2O$ molecules are held by hydrogen bonding to the $-NH_3^+$ groups but do not engage their own H atoms in any strong hydrogen bonding. This is consistent with the inference from the infrared spectrum as discussed earlier.

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# The Crystal and Molecular Structure of μ-Carbonyl-bis-μ-diphenylgermanium-bis(tricarbonyliron), $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$

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The structural determination by single-crystal X-ray methods of μ-carbonyl-bis-μ-diphenylgermanium-bis(tricarbonyliron), $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$, is described. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.705 \pm 0.004$ Å, $b = 10.916 \pm 0.004$ Å, $c = 13.702 \pm 0.005$ Å, $\alpha = 103° \ 19' \pm 4'$, $\beta = 96° \ 39' \pm 4'$, and $\gamma = 101° \ 53' \pm 3'$. There are two molecules per unit cell, calculated density 1.68 g $cm^{-3}$. The density measured by flotation is 1.70 ± 0.02 g $cm^{-3}$. A total of 1860 independent observations above background were collected by counter methods using crystal-monochromatized Mo Kα radiation. The structure was refined by least-squares methods to a conventional $R$ factor of 4.9%. Hydrogen atoms were included and the phenyl groups were refined using the rigid-body approximation. The molecule has two tricarbonyliron groups linked by an iron–iron bond of 2.666 (3) Å which is bridged by two diphenylgermanium groups and a carbonyl group. The Fe–Ge distances are in the range 2.402–2.440 Å and the Fe–Fe bond subtends 66.8° at the germanium atoms. There are small deviations in the symmetry of the bridge system. The germanium ligands are slightly closer to one iron atom and the carbonyl group is displaced slightly toward the other.

## Introduction

The crystal structure analysis of $[Ge(CH_3)_2]_3Fe_2(CO)_6$ has been described previously.[1] The structure proved to be based upon that of iron enneacarbonyl, with the three bridging carbonyl groups replaced by bridging dimethylgermanium groups. The Fe–Fe distance in the germanium-bridged complex was considerably longer than in the carbonyl, though short enough to imply an Fe–Fe bond. The preparation of a compound with formula $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$, postulated to contain an Fe–Fe bond bridged by two germanium atoms and a carbonyl group,[2] provided an interesting opportunity to obtain more information about the structural details of these germanium-bridged iron carbonyls. In particular, it seemed of interest to determine the effect of the bridging carbonyl group upon the Fe–Fe distance and the bridging angles of the germanium diphenyl ligands.

## Experimental Section

Crystals of $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$ were obtained as small red-black prisms. Preliminary photographs, both Weissenberg with Cu Kα radiation ($hk0$–$hk3$) and precession with Mo Kα radiation ($h0l$ and $0kl$), indicated a triclinic space group. Reciprocal cell parameters were taken from the precession photographs of levels ($h0l$) and ($0kl$), except for the angle $\gamma^*$ which came from measurements made with the diffractometer, with a crystal mounted about the $c$ axis.[3] Measurement of the precession photographs and the calculation of errors were performed according to Patterson and Love[4] and a sodium chloride ($a_{NaCl} = 5.6402$ Å) photograph on the same type of film was measured in the same way in order to calibrate the camera and to correct for film shrinkage. Final bond length calculations indicate that the cell parameter errors contribute about 25% of the error in an Fe–Ge distance. Final values for the real lattice parameters (λ 0.71069 Å, Mo Kα, 27°) are: $a = 10.705 \pm 0.004$ Å, $b =$

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(1) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1424 (1969).

(2) E. H. Brooks and W. A. G. Graham, to be submitted for publication.

(3) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1273 (1969).

(4) A. L. Patterson and W. E. Love, *Am. Mineralogist*, **45**, 325 (1960).