

Structure of Dichromium Tetraacetate by Gas-Phase Electron Diffraction

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Abstract: A gas-phase electron-diffraction study on the binuclear complex of chromium is reported. Scattered electron intensities were measured from vapors of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ produced in a quartz nozzle system at 200 °C. The measured metal-metal bond length, $r_a(\text{CrCr}) = 1.966$ (14) Å, compares remarkably well with the CrCr quadrupole bond value of 1.98 Å calculated by using the maximum valence radii of chromium. Our results differ from the X-ray structural parameters, thus showing that axial coordination and the presence of axial ligands strongly influence the bonding nature of Cr atoms in the binuclear complexes of chromium.

In the early 1960s the existence of double,¹ triple,² and quadruple³ bonds between transition-metal atoms was recognized. Since that time the interest in the chemistry of multiple metal-metal bonds has increased dramatically. There are more than 900 known compounds containing metal-metal bonds of the order 2-4 of which over 300 have been structurally characterized by X-ray crystallography.⁴ The metal-metal bond lengths in such compounds range from 1.83 to 2.72 Å.

Important differences have been noticed in the metal-metal bond lengths of the binuclear complexes of transition metals belonging to the same group in the periodic table. The metal-metal bond length in complexes of molybdenum ranges from 2.04 Å in $\text{Mo}_2[\text{pyNC}(\text{O})\text{CH}_3]_4$ ⁵ to 2.18 Å in $\text{Mo}_2(\text{C}_3\text{H}_5)_4$.^{6,7} This small variation in the bond lengths suggests that in the case of molybdenum complexes, the presence of axial ligands does not significantly influence the bonding character of the metal atoms. The situation is not so simple in the case of binuclear complexes of chromium. The metal-metal bond length shows a much wider variation, from a super short value of 1.847 Å in $\text{Cr}_2(6\text{-Me-2-MeOC}_6\text{H}_3)_4$ to a very long value of 2.541 Å in $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$.⁸ This wide variation can be explained by the perturbing effects on the axial ligands on the bonding character of Cr atoms. In the case of the dichromium tetraacetate the Cr-Cr bond length is 2.362 Å for the dihydrate crystal and 2.228 Å for the anhydrous crystal.⁹ Even in cases where no axial ligands are present, the molecular orientation in the crystal is such that the oxygen atoms from one molecule are situated very nearly axially to the Cr-Cr bond in the neighboring molecule. The resulting axial coordination interferes with the Cr-Cr bond much like the attached axial ligands.

Intense computational efforts have helped little to further the understanding of the Cr-Cr multiple bond. Most calculations were carried out assuming that the molecular structure parameters determined by X-ray diffraction can be transferred to the free molecule. For $\text{Cr}_2(\text{O}_2\text{CH})_4 \cdot 2\text{H}_2\text{O}$ this led to a nonbonded Cr-Cr potential in the Hartree-Fock approximation¹⁰ potential and to a very shallow minimum for some limited CI results.

Attempts to use the calculations to explain the photoelectron spectra¹¹ of the gaseous sample had to fail because the molecule releases the water at a much lower temperature than needed to produce sufficient vapor pressure in the sample chamber. In addition, there is a high probability that the anhydrous compound itself decomposed and the spectra were falsified by the volatile fragments.

There is no vibrational spectroscopic data on $\text{Cr}_2(\text{O}_2\text{CR})_4$ -type compounds, gaseous or solid. The theoretical result predicts the existence of a very shallow minimum in the Cr-Cr force field, implying very closely spaced vibrational levels and a difficult assignment of spectral lines without isotope substitution. In order to understand the nature of the Cr-Cr bond in binuclear complexes of chromium, it is important to characterize the gas-phase structure of the complex. At present, this is possible with the help of gas-phase electron diffraction. This expectation is based on the successful determination of the molecular structure of $\text{Mo}_2(\text{O}_2\text{-CCH}_3)_4$ in the gas phase in our laboratory.¹²

Experimental Section

Our diffraction unit has been described elsewhere in detail,¹³ so only the modifications required in this study will be presented here.

Dichromium tetraacetate presented a particular problem of vaporizing the compound. Attempts were made, in our laboratory, to obtain electron diffraction patterns of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ beginning in 1979. All past attempts met with frustrating results. The problems with this compound are twofold: Dichromium tetraacetate is very reactive and starts decomposing in the presence of air, and normal nozzle materials like copper. In all previous attempts using standard nozzle materials, the compound decomposed at about 100 °C, before a sufficient vapor pressure was reached.

Crystals of the compound were grown in a quartz apparatus by distilling at about 225 °C. It was recognized that by using a quartz nozzle in our electron diffraction chamber, it would be possible to heat the compound to over 200 °C, thus expecting sufficient vapor pressure to perform the experiment. Samples of anhydrous $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, prepared by Dr. Wenning Wang,¹⁴ were sealed into the quartz nozzle assembly by dipping the nozzle tip in molten camphor. They were transported in a container saturated with camphor vapor and opened by pumping off the camphor in the diffraction chamber at room temperature.

Scattered electron intensities were measured in an angular range of about 3°-10° on either side of the incident electron beam.¹⁵ When the diffraction patterns of gaseous SF_6 were used, the electron beam energy was calculated to be 41418 eV. The angular range thus corresponded to $s = 6.25\text{-}21.25 \text{ \AA}^{-1}$. A total of 14 independent diffraction patterns were obtained for this compound. This corresponded to a total of 745

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(14) W. Wang, Department of Chemistry, Texas A&M University, provided the samples of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

(15) See AIP document PAPS-XXXX-XXX for pages of the experimental intensities, theoretical molecular scattering curve, and the background for $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

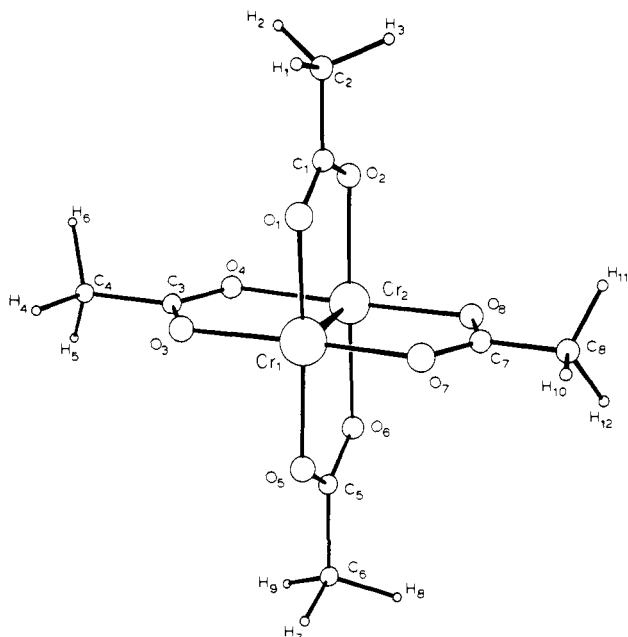


Figure 1. Molecular structure of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$.

data points. The compound was vaporized at about 200 °C. At this temperature dichromium tetraacetate has a very low vapor pressure (estimated at a few millitorrs), and accordingly the scattered electron intensities were very low. The temperature could not be increased because of the fear that the compound might break apart. Consequently there was a rather large scatter in the data, and it was necessary to average the 14 diffraction patterns. A simple window-averaging procedure with a variable window size of 0.15–0.25 \AA^{-1} was used to check the sensitivity of the final results to the window size. As a result of this averaging procedure, 54 data points were obtained which were treated as independent. The averaged data were interpolated in steps of 0.25 \AA^{-1} to suit the least-squares program. Noninterpolated data were also used in the least-squares refinement, and it was heartening to see them yield the same results, although with a larger standard deviation. This is due to the fact that interpolation necessarily smooths the data, thus having an averaging-like effect.

Data Reduction and Refinement of the Molecular Structure

The refinement of the molecular structure is based on programs developed by K. and L. Hedberg.^{16,17} A theoretical molecular scattering curve, $sM^{\text{th}}(s)$, is fit to prelevelled intensity curves obtained by subtracting a background from the experimental cross sections. This background is due to the part of the residual scattering which was not subtracted in the preliminary analysis and is usually less than 1% of the total scattering intensity.

Figure 1 illustrates the molecular geometry of dichromium tetraacetate. The geometry was assumed to be of C_{4h} symmetry and hence described by seven independent parameters, namely, $r(\text{CrCr})$, $r(\text{CrO})$, $r(\text{CO})$, $r(\text{CC})$, $r(\text{CH})$, $\angle\text{CrCrO}$, and $\angle\text{CCH}$. These seven parameters were used to calculate the nonequivalent interatomic separations needed in the least-squares refinement. The CrCr and the CrO distances could not be clearly resolved, and it was found best to specify the structure in terms of the average of and the difference between these two distances ($\text{CRAVG} = (r(\text{CrCr}) + r(\text{CrO}))/2$ and $\text{CRDIF} = r(\text{CrO}) - r(\text{CrCr})$). All hydrogen-containing distances except for the nearest neighbor distances were excluded from the model. This did not hamper the analysis because of the low scattering power of H. The CH bonded distance was fixed at 1.14 \AA , and $\angle\text{CCH}$ in the methyl group was fixed at 110°. As a result of this, 24 nonequivalent distances and their associated mean amplitudes of vibration were in the refinement procedure. These 24 distances were specified by the previously mentioned seven independent parameters. Figure 2 shows the experimental molecular scattering

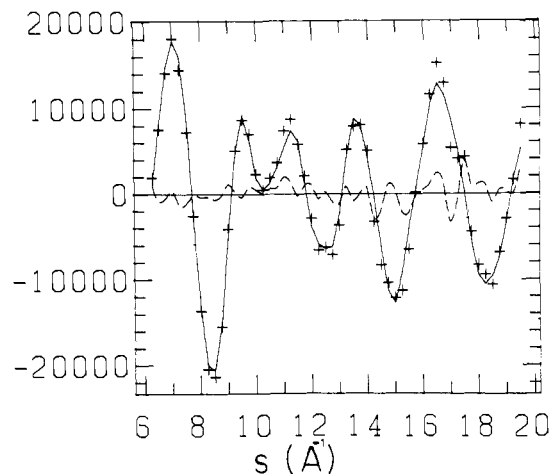


Figure 2. Experimental $sM(s)$ curves plotted vs. s . The crosses represent the interpolated averaged data. The solid line depicts the model calculated with the parameters given in Table II. The dotted line is the difference curve.

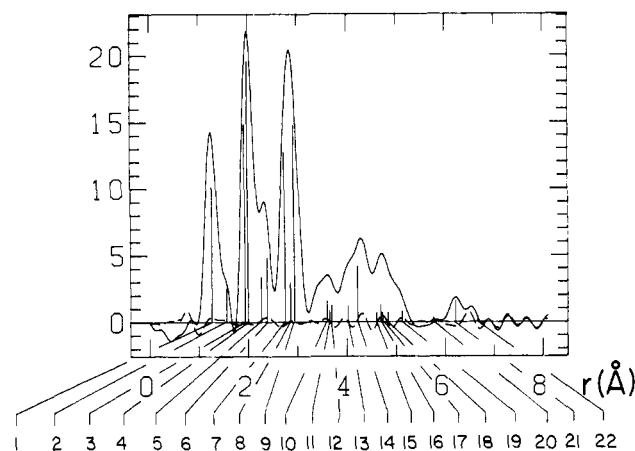


Figure 3. Experimental and difference radial distribution curves. The position of each vertical bar marks the internuclear separation of an atom pair. The length of the bar represents the scattering power, $n_{ij}Z_iZ_j/r_{ij}^4$. The numbers on the bars are identified in Table II.

Table I. Results for Dichromium Tetraacetate^a

| parameter | this study | X-ray study | |
|----------------------|------------|---|--|
| | | $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ | $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot (\text{H}_2\text{O})_2$ |
| CRAVG | 1.990 (4) | 2.160 | 2.196 |
| CRDIF | 0.047 (11) | -0.255 | -0.332 |
| CO | 1.267 (5) | 1.258 | 1.265 |
| CC | 1.525 (16) | 1.528 | 1.490 |
| $\angle\text{CrCrO}$ | 94.49 (34) | 87.7 | 88.04 |
| CrCr | 1.966 (14) | 2.288 | 2.362 |
| CrO | 2.014 (8) | 2.033 | 2.030 |
| R | 0.68 | | |
| σ | 0.14 | | |

^a All distances in angstroms, angles in degrees. The values in parentheses are estimates of 2σ .

curve together with the final model calculation and their differences. In this figure the problems due to the low vapor pressure and consequently the low count rates are visible in the large scatter in the difference curve. Figure 3 depicts the experimental radial distribution curve along with the difference curve in relation to the final fit to the equation for $sM^{\text{th}}(s)$.

The parameter values for the starting model were chosen from the results of the X-ray study.⁷ The initial values for the amplitudes were chosen from chemical intuition because of the total lack of any spectroscopic data on this compound. Far too many amplitudes of vibration are required in the analysis; therefore,

(16) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* 1964, 17, 529.

(17) The program used in the least-squares refinement was developed by K. Hedberg and L. Hedberg at Oregon State University.

Table II. Final Results of the Present Study^a

| bar label in Figure 2 | parameter | r_a | l |
|--------------------------|---------------------------------|------------|-----------|
| | C ₂ H ₁ | 1.14 | 0.07 |
| 1 | C ₁ O ₁ | 1.267 (5) | 0.064 (6) |
| 2 | C ₁ C ₂ | 1.525 (16) | 0.077 (8) |
| | H ₁ H ₂ | 1.743 | 0.13 |
| 3 | Cr ₁ Cr ₂ | 1.966 (14) | 0.04 (1) |
| 4 | Cr ₁ O ₁ | 2.014 (8) | 0.08 (1) |
| | C ₁ H ₁ | 2.293 (14) | 0.095 |
| 5 | O ₁ O ₂ | 2.282 (12) | 0.068 |
| 6 | O ₁ C ₂ | 2.369 (12) | 0.068 |
| 7 | Cr ₁ C ₁ | 2.743 (8) | 0.068 |
| 8 | O ₁ O ₃ | 2.840 (12) | 0.135 |
| 9 | Cr ₁ O ₂ | 2.924 (5) | 0.074 |
| 10 | O ₁ C ₃ | 3.621 (12) | 0.24 |
| 11 | C ₁ C ₃ | 3.648 (9) | 0.24 |
| 12 | O ₁ O ₄ | 3.644 (14) | 0.24 |
| 13 | O ₁ O ₅ | 4.017 (16) | 0.15 |
| 14 | Cr ₁ C ₂ | 4.202 (14) | 0.14 |
| 15 | O ₁ O ₆ | 4.620 (18) | 0.28 |
| 16 | O ₁ C ₄ | 4.693 (16) | 0.28 |
| 17 | O ₁ C ₅ | 4.709 (13) | 0.28 |
| 18 | C ₁ C ₄ | 4.821 (16) | 0.26 |
| 20 | C ₂ C ₄ | 5.778 (24) | 0.21 |
| 19 | C ₁ C ₅ | 5.121 (16) | 0.17 |
| 21 | O ₁ C ₆ | 6.200 (22) | 0.08 |
| 22 | C ₁ C ₆ | 6.646 (20) | 0.09 |
| | C ₂ C ₆ | 8.171 (34) | 0.10 |

^aAll distances and amplitudes are in angstroms. The values in parentheses are estimates of 2σ . Where no σ values are given, the parameter was fixed.

Table III. Correlation Matrix for Important Parameters of Dichromium Tetraacetate

| | σ | | | | | |
|---------|----------|--------|--------|-------|--------|--------|
| CRAVG | 0.002 | 1.000 | | | | |
| CRDIF | 0.007 | 0.610 | 1.000 | | | |
| CO | 0.002 | 0.466 | -0.743 | 1.000 | | |
| l(CrCr) | 0.01 | 0.747 | 0.336 | 0.034 | 1.000 | |
| l(CrO) | 0.01 | 0.721 | -0.708 | 0.445 | 0.456 | 1.000 |
| ∠CrCrO | 0.17 | -0.741 | 0.889 | 0.528 | -0.396 | -0.321 |

they were arranged in groups. The differences between them were maintained during the least-squares fit procedure. The ordering of the mean amplitudes of vibration is shown in Table II. No attempt was made to use either the anharmonicity parameter or the shrinkage corrections while enforcing a rigid D_{4h} symmetry.

The final results of the present study are listed in Table I along with the results of two X-ray studies, one on hydrous acetate and the other on the anhydrous acetate. Table II lists the values of all parameters resulting from our study. Table III lists the correlation matrix for some important parameters, with coefficients > 0.4 , used in the least-squares refinement. In spite of the high correlation between CRAVG and CRDIF, a $r(\text{CrO})$ value of 2.014 (8) Å compares well with the X-ray value of 2.033 Å in anhydrous acetate and 2.030 Å in hydrous acetate.

The Cr–Cr bond length resulting from the present study, 1.966 (14) Å, is substantially shorter than either of the X-ray values. This confirms the strong influence of axial ligands and axial coordination on the bonding nature of chromium atoms in the binuclear complexes of chromium. Pauling^{4,18} has used maximum valence radii concepts to calculate the length of the quadrupole bond between transition-metal atoms. The length of the Cr–Cr quadruple bond thus calculated is 1.98 Å, which agrees remarkably well with our results. Similar calculations on quadruple Mo–Mo and Re–Re bonds also agree well with experimental results.

It is relatively difficult to interpret the mean amplitudes of vibration emerging out of the present experiment. They represent some sort of an average amplitude for all the distances falling

under the same peak in the radial distribution curve. Lack of any knowledge about shrinkage corrections compounds this problem, especially for large internuclear separations. In spite of this it is still possible to attach some significance to the amplitudes corresponding to the bonded distances.

The mean amplitude of vibration for a diatomic molecule is related to the vibrational frequency, in the harmonic approximation and for a Boltzmann distribution, by

$$l^2 = \frac{h}{8\pi^2\mu c\omega} \coth\left(\frac{hc\omega}{kT}\right)$$

where μ is the reduced mass and ω is the vibrational frequency in inverse centimeters. Moreover, in a harmonic approximation the vibrational frequency is related to the force constants by

$$f_c = 4\pi^2c^2\omega^2\mu$$

The values of the amplitude of vibration for the Cr–Cr and Cr–O bonds are $l(\text{Cr–Cr}) = 0.04$ Å and $l(\text{Cr–O}) = 0.08$ Å, respectively. This translates into force constants of $f_c(\text{Cr–Cr}) = 3.8$ mdyn/Å and $f_c(\text{Cr–O}) = 1.0$ mdyn/Å. A value of 1 mdyn/Å for the force constant for the Cr–O bond seems like a reasonable one, especially in view of the fact that the force constant for the Mo–O bond in an analogous compound (dimolybdenum tetraacetate) is 1.1 mdyn/Å.

Woodruff¹⁹ has compiled all the available data on bond lengths and force constants for the dimeric bonds of all group 4 elements. There is an approximate exponential relation between the two quantities. Our results of $r(\text{Cr–Cr}) = 1.966$ Å and $f_c(\text{Cr–Cr}) = 3.8$ mdyn/Å agree well with the other values. The results mentioned above have to be viewed with some caution in view of the fact that the index of resolution was refined to a rather low value of 0.68. This low value could be the result of some decomposition of the compound. We cannot compare our results to the theoretical computations because all were carried out for compounds containing an attached ligand and frozen X-ray structure parameters. Computations should be carried out on $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ using our values of the structure parameters.

The force constants derived from the mean amplitudes of vibrations predict a strong potential minimum with a vibrational energy level not much different from those of the Mo compound. Therefore, matrix isolation vibrational spectroscopy seems to be ideally suited to measure the spectra, minimizing the axial bond distortion and giving force constants which could be used for a reanalyzed structure study based on the present data sets.

The result obtained here confirms the conclusion of Cotton and Walton²⁰ based on analyses of structural data for a number of dichromium molecules. In order to prove that the Cr–Cr distance is unusually sensitive to the axial environment, new molecules were investigated where the RCO_2 groups were replaced by either triazines, amidinates, or amidates. These bridging structures enable the attachment of ligands of such a size that the axial Cr–Cr bond is stereochemically shielded from further next-neighbor interference. Table 4.2.3 in ref 4 clearly shows the shrinking of the Cr–Cr distance as the substituted groups grow larger. However, a new controversy arose concerning the influence of the electron density redistribution in these N compounds. Therefore, only a direct structure measurement of the free and isolated $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ could resolve these issues. Our bond length of 1.966 (14) Å for the Cr–Cr pair shows that the short distance occurs naturally and that all axial ligands perturb the electron distribution significantly and thus stretch the bond.

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Registry No. $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, 15020-15-2.

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