Communications to the Editor

A Neutron Diffraction Study of $[Et_4N]^+[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$: a $[M_2(CO)_{10}(\mu_2\text{-}H)]^-$ Monoanion with a Pseudo D_{4h} Nonhydrogen Geometry Together with a Disordered, Bent Symmetric Metal–Hydrogen–Metal Bond[1]

Sir:

We wish to report the results of a single-crystal neutron diffraction study of the chromium-hydrogen-chromium bond in $[Et_4N]^+[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$, which on the basis of an earlier x-ray diffraction study[2] was presumed to be the first example of a linearly protonated metal-metal bond. In conjunction with our previous neutron diffraction analysis of the bent three-center, electron-pair bond in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu_2\text{-}H)$ $(\mu_2\text{-}P(CH_3)_2)$,[3] this investigation was undertaken to substantiate the presumed linearity of the Cr–H–Cr linkage in the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion as well as to obtain stereochemical information about the nature of the Cr–H–Cr interaction.[4,5] Due to the intrinsic limitations of the x-ray photographic experiment, the position of the bridging hydrogen atom in the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion was not directly determined, but its proposed location along the metal–metal axis was based upon the idealized D_{4h} geometry of the nonhydrogen atoms, the crystallographic $C_i\text{-}\bar{1}$ symmetry imposed upon the entire monoanion, and the assumption that the metal-coordinated hydrogen atom occupies a regular metal coordination site.[2] It was thereby presumed[2] that the bridging hydrogen atom either lies on the crystallographic center of symmetry, equidistant from the symmetry-related metal atoms (corresponding to its being in a symmetric single-minimum potential well), or is statistically averaged due to its random distribution over equivalent sites displaced from the center of symmetry along the metal–metal axis (corresponding to its being in a symmetric double-minimum potential well). The outcome of our neutron diffraction study of the Cr–H–Cr bond in the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion of the tetraethylammonium salt is completely unanticipated in that the Cr–H–Cr bond is found at room temperature to be *nonlinear* with the bridging hydrogen atom randomly disordered between *two* centrosymmetrically related sites each equidistant (within experimental error) from the two chromium atoms and displaced ca. 0.3 Å from the crystallographic center of symmetry.

Suitable crystals[6] of $[Et_4N]^+[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ were grown by a slow removal of the solvent from a saturated ethanol solution placed over magnesium perchlorate in a N_2-filled desiccator. A well-formed yellow crystal of approximate volume 19.2 mm³ and weight 21.93 mg was sealed in a lead-glass capillary and mounted on the Chemistry Division neutron diffractometer at the CP-5 reactor. A least-squares fit of 30 automatically centered reflections ($40° < 2\theta < 60°$) confirmed the triclinic unit cell ($P\bar{1}$) with a = 6.799 (2) Å, b = 10.105 (4) Å, c = 8.893 (4) Å, α = 101.70 (2)°, β = 101.72 (2)°, γ = 86.16 (2)°, V = 585.4 Å³, and d_{calcd} = 1.462 g cm^{-3} for Z = 1. Integrated intensities of 3325 Bragg reflections (λ 1.142 Å) from four independent octants of the reciprocal lattice were measured at 22 ± 2 °C. After an absorption correction (i.e., μ = 1.59 cm^{-1} with minimum and maximum transmission coefficients of 0.66 and 0.77, respectively), the equivalent reflections were averaged to give 2922 independent data. A least-squares isotropic refinement[7,8] performed on the nonhydrogen atomic coordinates obtained from the x-ray diffraction study provided sufficient phase information to locate the remaining hydrogen atoms from a difference Fourier analysis. At this point two centrosymmetrically related peaks corresponding to a disordering of the bridging hydrogen atom were clearly resolved. A full-matrix least-squares anisotropic refinement of the crystallographically independent unit consisting of one chromium atom, five carbonyl groups, a half-weighted bridging hydrogen atom, and a disordered tetraethylammonium cation[9] ultimately led to final discrepancy indices[10] of $R(F_o)$ = 0.072, $R(F_o^2)$ = 0.065, and $R_w(F_o^2)$ = 0.074 with σ_1 = 1.09 for 2050 reflections with $F_o^2 > 1.0\sigma(F_o^2)$.

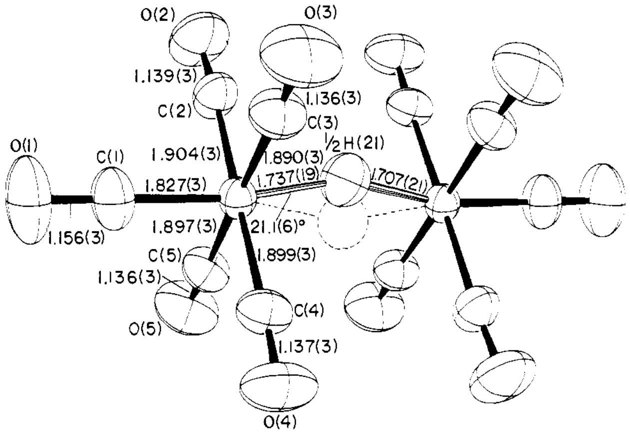


Figure 1. Architecture of the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion of crystallographic $C_i\text{-}\bar{1}$ symmetry showing the approximate D_{4h} geometry of the dichromium decacarbonyl framework and the two centrosymmetrically related (half-weighted) sites of the bridging hydrogen atom in the bent Cr–H–Cr fragment. The thermal ellipsoids of nuclear motion for all atoms are scaled to enclose 50% probability. Internuclear distances and bond angles are given with their estimated standard deviations.

The determined configuration of the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion is illustrated in Figure 1, which depicts the approximate D_{4h} geometry of the dichromium decacarbonyl framework, together with the two centrosymmetrically related disordered sites of the hydrogen atom in the bent Cr–H–Cr fragment. The significant displacement of the two half-weighted hydrogen positions by ca. 0.3 Å from the crystallographic center of symmetry gives rise to a nonlinear Cr–H–Cr bond angle of 158.9 (6)°. A symmetric disposition of the bridging hydrogen atom about the two chromium atoms is indicated from the experimentally equivalent Cr–H internuclear distances of 1.707 (21) and 1.737 (19) Å. For a presumed linear Cr–H–Cr bond with the hydrogen atom positioned on the center of symmetry, the observed Cr–Cr distance of 3.386 (6) Å would give rise to two identical Cr–H bond lengths of 1.693 Å.

Another view of the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion approximately along the Cr–Cr axis is illustrated stereoscopically in Figure 2, which clearly shows that the two co-planar, bent Cr–H–Cr moieties are staggered[11] with respect to the eclipsed array of equatorial carbonyl ligands. As was previously found for the bridging H atom in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu_2\text{-}H)$-$(\mu_2\text{-}P(CH_3)_2)$, the maximum root mean square component of thermal displacement (viz., $\mu(3)$ = 0.441 (11) Å) for the bridging H atom in $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ is also directed ap-

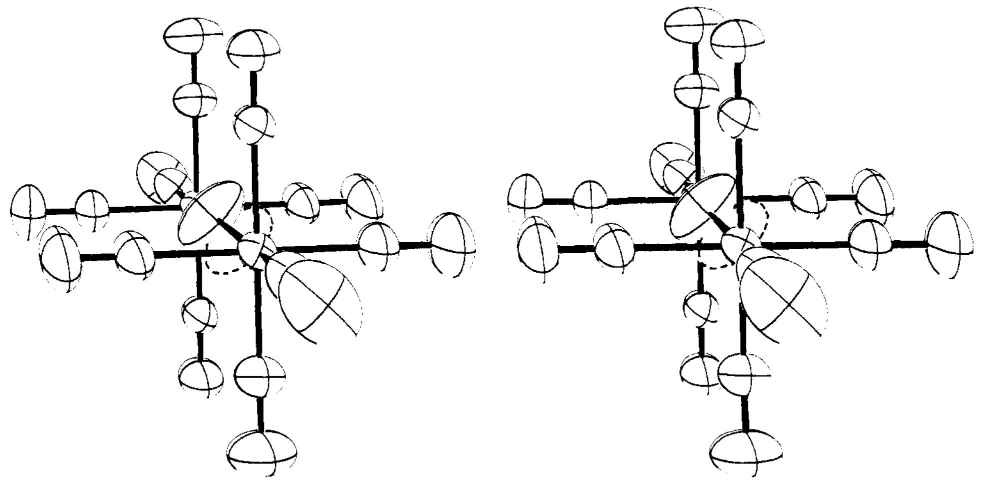
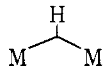


Figure 2. Stereoscopic drawing of the $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion as viewed approximately along the Cr-Cr axis. The Cr-H-Cr plane is staggered with respect to the eclipsed array of equatorial carbonyls. The thermal anisotropy of the bridging hydrogen atom is primarily directed normal to the Cr-H-Cr plane. In harmony with an analysis of the nuclear thermal ellipsoids, this particular view indicates that the observed thermal anisotropy of the axial carbonyl atoms is consistent with these whole-weighted atomic sites actually being a composite of two nearly superimposed orientations of a slightly bent $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ structure of idealized C_{2v}-*mm*2 geometry. The complete resolution of the two half-weighted hydrogen sites is attributed to a closed-type bond such as I, where M = Cr.

proximately normal to the M-H-M plane (viz. 85 (4)°). Although the hydrogen disorder is not sufficient to alter the overall pseudo D_{4h} geometry of the metal carbonyl framework, a detailed examination of the sizes, shapes, and orientations of the nuclear thermal ellipsoids of the axial carbonyl atoms provides convincing evidence that the observed nonhydrogen structure is the result of a crystal disorder involving the near superposition of two slightly bent identical $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ structures of idealized C_{2v}-*mm*2 geometry. An analysis[12,13] of the nuclear thermal ellipsoids of the axial carbonyl atoms yields estimated displacements of ca. 0.08 Å for the two half-weighted carbon atoms and ca. 0.15 Å for the two half-weighted oxygen atoms from their respective neutron determined composite positions. The fact that the magnitudes of these estimated displacements are smaller than the ca. 0.3 Å displacements of the completely resolved, half-weighted hydrogen atoms from the centrosymmetric midpoint of the direct Cr-Cr line is in accord with the bridging hydrogen atom not being positioned at an octahedral metal coordination site but instead displaced such that the three-center, electron-pair Cr-H-Cr interaction is a closed-type



I

bond.[14] These results thereby support the premise that the bridging hydrogen atoms in bent M-H-M fragments are unlike terminal hydrogen atoms in that they do not occupy regular metal coordination sites.

The deformability of the $[M_2(CO)_{10}(\mu_2\text{-}H)]^-$ species to adopt a considerably bent, staggered carbonyl structure was first uncovered by Bau and co-workers[14] from neutron diffraction studies of two crystalline modifications of the electronically equivalent neutral $W_2(CO)_9(NO)(\mu_2\text{-}H)$ molecule. They subsequently found from x-ray diffraction studies[15] that the *nonhydrogen* backbone of the isoelectronic $[W_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion also has a similarly bent structure in the bis(triphenylphosphine)iminium salt but a linear structure in the tetraethylammonium salt with the W-W separation being 0.11 Å less in the bent form. They suggested[15] that crystal-packing forces are probably responsible for determining the configuration of the monoanion in the solid state. The observation[15] that all known salts of the $[W_2(CO)_{10}(\mu_2\text{-}H)]^-$ monoanion exhibit the same three-band infrared solution pattern of carbonyl absorptions (indicating the existence of only the slightly bent nonhydrogen configuration in solution) suggests an inherent stability of the eclipsed carbonyl geometry. One may conclude that the potential energy surface associated with the hydrogen nucleus is sufficiently shallow to facilitate an easy bending of the Cr-H-Cr fragment without sufficiently perturbing the carbonyl ligands to allow them to undergo a twisting distortion toward a staggered bent geometry.

These neutron results suggest the distinct possibility that a bent rather than a linear M-H-M fragment also exists in the pseudo D_{4h} nonhydrogen geometry of the molybdenum and tungsten monoanions in the tetraethylammonium salts[15] and of the chromium monoanion in the bis(triphenylphosphine) iminium salt.[16,17] In an effort to provide more definitive structural information needed to permit unambiguous interpretations of the spectroscopic properties[6,15,18] of this intriguing series of complexes, neutron diffraction studies of $[(PPh_3)_2N]^+[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ and $[Et_4N]^+[Mo_2(CO)_{10}(\mu_2\text{-}H)]^-$ are currently underway.

Supplementary Material Available: A listing of atomic coordinates and structure factor tables (15 pages). Ordering information is available on any current masthead page.

References and Notes

(1) This work was performed under the auspices of the U.S. Energy Research and Development Administration. We are pleased to acknowledge partial support of the initial stages of this work by a grant from Research Corporation. Acknowledgments are also gratefully made for partial support of this research by L.F.D. and J. M. W. to the National Science Foundation (Grant No. CHE76-07409). J.R. (presently at the Laboratoire des Acides Mineraux, Université des Sciences et Techniques du Languedoc, Place Eugene Bataillon, 34060 Montpellier, Cedex, FRANCE) is indebted to the National Science Foundation and the Centre National de La Recherche Scientifique for the award of a program exchange grant.

(2) (a) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 366 (1966); (b) L. B. Handy, J. K. Ruff, and L. F. Dahl, *ibid.*, **92**, 7312 (1970).

(3) J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Am. Chem. Soc.*, **96**, 6610 (1974).

(4) An intrinsic uncertainty problem[5] is encountered in an accurate determination of the nuclear position of the hydrogen atom by diffraction methods when special crystallographic site symmetry (such as an inversion center) is imposed at the hydrogen atom.

(5) (a) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W.A. Benjamin, New York, N.Y., 1968; (b) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am Chem. Soc.*, **89**, 4323 (1967); (c) J. C. Speakman, *Struct. Bonding (Berlin)*, 12, 166 (1972).

(6) This compound was prepared via a procedure given elsewhere (R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966)).

(7) All least-squares refinements were based on the minimization of $\Sigma w_i|F_o^2 - S^2F_c^2|^2$ with the individual weights $w_i = 1/\sigma^2(F_o^2)$. The neutron scattering amplitudes used[8] in this study are $b_{Cr} = 0.352$, $b_N = 0.940$, $b_C = 0.663$,

$b_O = 0.580$, and $b_H = -0.374$ (all units in 10^{-12} cm).

(8) G. E. Bacon, *Acta Crystallogr., Sect. A*, **28,** 357 (1972).

(9) The disordered model previously used by the x-ray diffraction study[2] for the carbon atoms of the tetraethylammonium cation is considerably improved due to the higher resolution of the neutron diffraction data. The cation is randomly distributed between two centrosymmetrically related orientations with no accompanying superimposed positioning of the methyl carbon atoms. All of the half-weighted carbon and hydrogen atoms in the monocation were located and refined in the neutron diffraction study.

(10) $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R(F_o^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$, $R_w(F_o^2) = [\Sigma w_i|F_o^2 - F_c^2|^2/\Sigma w_i F_o^4]^{1/2}$. σ_1, the standard deviation of an observation of unit weight, is defined by $[\Sigma w_i|F_o^2 - F_c^2|/(n-p)]^{1/2}$ where $w_i^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_c^2) + (0.02F_o^2)^2$; σ_c is determined by counting statistics, n denotes the number of observations, and p denotes the number of parameters varied during the least squares.

(11) The plane of each of the two coplanar Cr–H–Cr fragments is oriented at angles of 44.2 and 45.9° with respect to the two perpendicular mean planes each passing through the two chromium atoms and the two axial and four equatorial ligands.

(12) In contrast to the direction of $\mu(3)$ for the bridging hydrogen atom, the maximum rms components of thermal displacement for the axial carbon and oxygen atoms (*viz.*, $\mu(3) = 0.287(3)$ Å and $\mu(3) = 0.391(4)$ Å, respectively) are directed essentially parallel to the Cr–H–Cr plane and normal to the Cr–Cr line. The acute angles between the direction of $\mu(3)$ for the bridging hydrogen atom and $\mu(3)$ for the axial carbon and oxygen atoms are 86 (4)° and 87 (4)°, respectively.

(13) The estimated displacements were based upon the assumption that the two half-weighted carbon and two half-weighted oxygen atoms can be represented with isotropic thermal displacement of 0.20 and 0.24 Å, respectively; each of these values is approximately equal to the mean value of the thermal displacements of the composite peak normal to the corresponding maximum displacement, $\mu(3)$.

(14) (a) M. Andrews, D. L. Tipton, S. W. Kirtley, and R. Bau, *J. Chem. Soc., Chem Commun.*, 181 (1973); (b) J. P. Olsen, T. F. Koetzle, S. W.Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96,** 6621 (1974).

(15) R. D. Wilson, S. A. Graham, and R. Bau, *J. Organomet. Chem.*, **91,** C49 (1975).

(16) In contrast to the x-ray determined bent nonhydrogen geometry of the monoanion in $[(Ph_3P)_2N]^+[W_2(CO)_{10}(\mu_2\text{-}H)]^-$ [15,17] and in $[(Ph_3P)_2N]^+[Mo_2(CO)_{10}(\mu_2\text{-}H)]^-$,[15] the chromium monoanion in $[(Ph_3P)_2N]^+[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-$ was found from an x-ray diffraction study[17] to have a pseudo D_{4h} nonhydrogen framework essentially identical with that observed for the chromium monoanion in the tetraethylammonium salt.

(17) J. L. Petersen, J. P. O'Connor, J. K. Ruff, and L. F. Dahl, unpublished research, 1974.

(18) (a) U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965); *J. Am. Chem. Soc.*, **89,** 539 (1967); (b) W. F. Edgell and N. A. Paauwe, *Chem. Commun.*, 284 (1969); N. A. Paauwe, Ph.D. Thesis, Purdue University, 1968; (c) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72,** 231 (1972); S. W. Kirtley, Ph.D. Thesis, University of California at Los Angeles, Aug 1971; (d) D. C. Harris and H. B. Gray, *J. Am. Chem. Soc.*, **97,** 3073 (1975).

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Cadmium-113 Nuclear Magnetic Resonance Studies of ^{113}Cd(II)-Substituted Human Carbonic Anhydrase B

Sir:

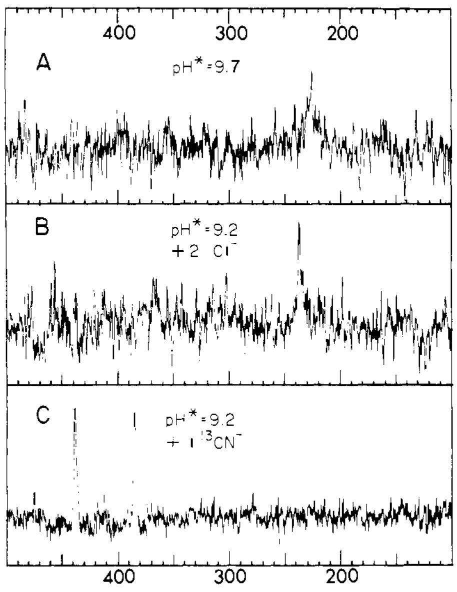

Figure 1. ^{113}Cd FT NMR spectra at 25 °C of 96% isotopically enriched ^{113}Cd^{II}HCAB in 85% H_2O/D_2O and 25 mM Tris sulfate. Chemical shifts (ppm) based on 1.0 M $CdSO_4$ at −2.8 ppm (ref 5a). No proton decoupling was employed. pH* values are uncorrected for presence of 15% D_2O. Exponential multiplication with 7 Hz line broadening was applied to the free-induction decays: (A) 5 mM enzyme, pH* 9.7, no inhibitors present, 12-h accumulation; (B) 7 mM enzyme, pH* 9.2, 2 equiv of NaCl added, 5-h accumulation; (C) above sample, plus 1 equiv of $K^{13}CN$ (90% isotopic enrichment), 10-h accumulation.

Carbonic anhydrases (carbonate hydrolyase EC 4.2.1.1) are zinc metalloenzymes found in animals, plants, and certain bacteria, which catalyze the reversible hydration of carbon dioxide ($CO_2 + H_2O = HCO_3^- + H^+$), the hydrolysis of certain esters, and various other reactions.[1] Carbonic anhydrases from human erythrocytes (HCA) are monomeric enzymes of molecular weight ~29 000, each molecule containing a single equivalent of firmly bound Zn(II) which is required for catalytic activity. X-ray crystallographic studies of the low-activity (HCAB)[2a] and high-activity (HCAC)[2b] isozymes reveal the zinc ions near the bottoms of 12–15 Å clefts, coordinated to nitrogen atoms from three histidyl side chains in distorted tetrahedral geometry, with the fourth coordination sites presumably occupied by water molecules or hydroxide ions. Kinetic studies on HCA point to the existence of two (or more) species per isozyme in acid-base equilibrium having pK_a values near 7, with the high-pH forms producing faster hydration rates. The identities of the various active species and the detailed mechanisms of their action remain in dispute.[3]

Direct observation by NMR of the metal at the active site of a metalloenzyme is expected to provide information regarding the chemical environment of the active site, free from the background interference characteristic of ^{1}H and ^{13}C NMR spectra of proteins. Advances in sensitivity of modern Fourier transform NMR spectrometers and the use of large (15–20 mm o.d.) sample tubes have made it possible to consider direct observation of individual atom resonances for millimolar enzyme solutions.[4] However, ^{113}Cd, with its spin quantum number $I = 1/2$, is expected to produce superior NMR spectra in a ^{113}Cd(II)-substituted enzyme over that of ^{67}Zn, with its lower gyromagnetic ratio and $I = 5/2$, with the resultant likelihood of quadrupole broadened resonances in the ^{67}Zn(II)-enzyme. Furthermore, it has been demonstrated that ^{113}Cd, like many heavy metals, exhibits a large chemical shift range (>600 ppm), making it potentially very sensitive to changes in the active site environment.[5]

Replacement of zinc ions by other divalent metal ions has often been used to provide spectroscopic probes of the active site of carbonic anhydrase. With the notable exception of Co(II), most divalent metal ions fail to restore much catalytic activity. Recently, however, it has been shown that Cd(II)-HCAB is an effective catalyst, at least for the hydrolysis of *p*-nitrophenylacetate, with a pK_a value of ~9.1 for the activity-linked functional group.[6]

Figure 1A shows the ^{113}Cd NMR spectrum[7] at 25 °C of 4 mL of ^{113}Cd(II)HCAB[8] at pH* 9.7 in the absence of mono-