at 120 °C for 3 h, during which time the solution was monitored by NMR spectroscopy. The above experiment was repeated with use of solutions that contained (η^5-$C_5H_5)_2Ni_2(p$-$CH_3C_6H_4C_2C_6H_4$-p-CH_3) and weighed amounts of diphenylacetylene (0.0627 g, 3.52×10^{-4} mol and 0.1255 g, 7.05×10^{-4} mol). The NMR tubes were placed in the NMR probe at 120 °C, and the ^{1}H NMR spectrum was monitored as a function of time (1-3 h); specifically line width changes and a separation of tetramethylsilane signals (capillary and solution) were sought.

Results and Discussion

Hydrogen did not react with $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ until temperatures slightly above 120 °C were reached at which point hydrogenation and gross decomposition occurred to give a nickel film on the walls of the reaction tube. With mixtures of 3-hexyne and hydrogen, there was no evidence of alkyne hydrogenation catalyzed by the dinuclear nickel acetylene complex at 120 °C, a temperature at which hydrogenative decomposition of the dinuclear complex was not detected. Alkyne exchange occurred at measurable rates between diphenylacetylene and $(C_5H_5)_2Ni_2(p$-$CH_3C_6H_4C_2$-p-$CH_3C_6H_4)$ at 120-150 °C. The alkyne-exchange reaction appeared to proceed through mononuclear reaction intermediates; see discussion below. Failure of the dimer to function as a catalyst for alkyne hydrogenation may be ascribed to coordination saturation in the dimeric nickel complex and to thermal reactivity of mononuclear fragments like C_5H_5NiH (possible precursor to nickel metal) resulting from the hydrogen reaction above 120 °C.

Alkyne exchange between free alkyne and the dinuclear metal alkyne complex could be rationalized by a number of plausible mechanisms. One pathway would be fragmentation to mononuclear complexes (eq 1) either through an associative

$$(C_5H_5)_2Ni_2(RC_2R) + R'C_2R' \rightleftharpoons C_5H_5Ni(RC_2R) + C_5H_5Ni(R'C_2R') \quad (1)$$

first step or through a dissociative set of reactions involving a first step of dissociation into C_5H_5Ni and $C_5H_5Ni(RC_2R)$ fragments. We attempted to establish whether fragmentation was occurring in these exchange reactions by using a mixture of ring-labeled dimers, $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ and $(CH_3C_5H_4)_2Ni_2(C_6H_5C_2C_6H_5)$. Scrambling occurred to give substantial amounts of $(C_5H_5)(CH_3C_5H_4)Ni_2(C_6H_5C_2C_6H_5)$ simply on mass spectrometric analysis of physical mixtures of the C_5H_5 and $CH_3C_5H_4$ dimers (mass spectrometer inlet at 90 °C). Thus, the alkyne-exchange reaction could not be monitored because of the extensive scrambling that occurred in the mass spectrometric analysis. However, the very fact that scrambling occurred so readily under relatively mild (thermal) conditions in the mass spectrometer suggests that alkyne exchange by fragmentation a la eq 1 is a reasonable reaction course. Also, it has been shown that $Co_2(CO)_8$ reacts with $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ at 70 °C to form substantial quantities (25% isolated yield) of $(C_5H_5)NiCo(CO)_3(\mu_2$-$C_6H_5C_2C_6H_5)$.[9]

The molecularity of the acetylene-exchange reaction in xylene solution was examined, and a rate expression of the form rate = $(k_1 + k_2[RC_2R])$[complex] (see Figures 1 and 2) was obtained with values for k_1 and k_2 of 1.62×10^{-3} min^{-1} and 1.5×10^{-3} L mol^{-1} min^{-1}, respectively. These data alone are mechanistically nondefinitive; the rate expression has the ubiquitous interchange form for reactions of transition-metal complexes. Collectively, however, the kinetic and chemical reactivity data are *suggestive* of a fragmentation pathway with the key intermediate a 17-electron species, $C_5H_5Ni(RC_2R)$. Competitive with this pathway would be interchange with the generation of $C_5H_5Ni(RC_2R)$ and $C_5H_5Ni(\eta^x$-p-xylene) species. Nevertheless, the alternative interchange sequence $[(C_5H_5)_2Ni_2(RC_2R)] + S\ (\text{solvent}) \rightleftharpoons [(C_5H_5)_2Ni_2S] + RC_2R$ cannot be excluded by our data. This alkyne-exchange reaction for the nickel dinuclear complex differs qualitatively from that based on $(C_5H_5)_2Mo_2(CO)_4(RC_2R)$ where fragmentation does not occur[1] and the initial, rate-determining step in exchange comprises dissociation of a CO ligand.

The suggested mononuclear intermediates for the acetylene-exchange mechanism would be paramagnetic. Attempts by NMR spectroscopy to detect such a species at 120 °C over several hour periods were unsuccessful for solutions of (η^5-$C_5H_5)_2Ni_2(p$-$CH_3C_6H_4C_2C_6H_4$-p-CH_3) and for solutions of this complex with 1 and 10 equiv of excess diphenylacetylene.[10] Clearly, such fragments, if they were responsible for the acetylene exchange process, must be present in low concentration at 120 °C, a feature not inconsistent with the relatively low rate of acetylene exchange in the reaction systems.

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Registry No. (η^5-$C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$, 35828-66-1; ($\eta^5$-$C_5H_5)_2Ni_2(C_2H_5C_2C_2H_5)$, 76096-33-8; ($\eta^5$-$C_5H_5)_2Ni_2$-$(CH_3C_6H_4C_2C_6H_4CH_3)$, 76529-88-9; $C_6H_5C_2C_6H_5$, 501-65-5.

Supplementary Material Available: A listing of kinetic data for the acetylene exchange reaction (1 page). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of a Substitution-Labile Chromium(III) Complex: Aquo(ethylenediaminetriacetatoacetic acid)chromium(III)

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Chromium(III) octahedral complexes are generally inert to the substitution of inner-sphere water molecules by other ligands. Recent reports indicate, however, the chromium(III) complexed with one water molecule and a five-coordinate EDTA-type ligand shows unexpectedly rapid substitution rates with several anionic ligands.[1,2] It has been suggested that these reaction rates are due in part to strains present in the complex.[3] The crystal and molecular structure determination of [Cr(H$_2$O)HEDTA] has been undertaken to ascertain the extent of distortion from octahedral geometry that is present in the molecule in the solid state. The crystal structure of [Cr(H$_2$O)HEDTA] has previously been shown to be isomorphous to the structure reported for Fe(III),[4] Ga(III),[4] and Rh(III)[5] complexes.

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Table I. Positional and Thermal Parameters and Their Standard Deviations in the Compound [Cr(H_2O)HEDTA]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.1970 (0)	0.8281 (0)	0.1429 (0)	1.23 (1)	1.22 (1)	1.31 (1)	0.08 (1)	0.15 (0)	−0.03 (1)
O(8)	0.3619 (2)	0.8408 (2)	0.2346 (0)	2.11 (8)	1.70 (7)	1.76 (6)	−0.01 (6)	−0.13 (5)	0.06 (5)
O(9)	0.0112 (2)	0.8502 (2)	0.1936 (0)	2.07 (8)	1.98 (7)	1.93 (6)	0.25 (6)	0.75 (5)	−0.13 (5)
O(7)	0.0537 (2)	0.8127 (2)	0.0410 (0)	1.16 (7)	2.13 (7)	1.55 (6)	0.20 (5)	0.28 (5)	−0.13 (5)
O(6)	0.2256 (2)	1.0491 (2)	0.1245 (1)	1.75 (8)	1.22 (6)	3.04 (8)	0.03 (5)	−0.38 (6)	0.07 (5)
N(2)	0.1743 (2)	0.6090 (2)	0.1760 (1)	1.46 (8)	1.56 (7)	1.47 (7)	−0.01 (6)	0.14 (6)	0.06 (6)
N(1)	0.3679 (2)	0.7389 (2)	0.0772 (1)	1.12 (7)	1.36 (7)	1.59 (7)	−0.02 (6)	0.05 (6)	−0.01 (6)
O(5)	0.4841 (3)	0.7117 (2)	0.3377 (1)	2.74 (10)	3.41 (9)	2.24 (7)	−0.21 (7)	−0.89 (6)	0.48 (6)
O(4)	0.6700 (3)	0.6656 (2)	0.0245 (1)	2.13 (8)	2.65 (8)	3.63 (9)	−0.14 (7)	1.18 (7)	−1.12 (7)
O(3)	0.7516 (2)	0.9057 (2)	0.0495 (1)	1.50 (7)	2.05 (7)	3.51 (8)	−0.12 (6)	0.78 (6)	0.11 (6)
O(2)	0.0382 (2)	0.7789 (2)	−0.0857 (0)	1.99 (8)	3.15 (8)	1.46 (6)	0.68 (7)	−0.36 (5)	−0.21 (5)
O(1)	−0.2023 (3)	0.7258 (2)	0.2234 (1)	1.96 (8)	3.49 (9)	3.55 (9)	0.42 (8)	1.41 (7)	0.37 (7)
C(5)	0.2581 (4)	0.5966 (3)	0.2580 (1)	2.24 (11)	2.24 (11)	1.74 (10)	−0.21 (9)	−0.22 (8)	0.60 (8)
C(6)	0.3789 (3)	0.7228 (3)	0.2799 (1)	2.14 (11)	2.36 (9)	1.57 (9)	0.21 (9)	0.06 (8)	−0.04 (7)
C(7)	−0.0036 (3)	0.5839 (3)	0.1704 (1)	1.46 (9)	1.87 (10)	2.06 (10)	−0.20 (7)	0.44 (7)	0.17 (7)
C(8)	−0.0741 (3)	0.7288 (3)	0.1993 (1)	1.78 (10)	2.62 (10)	1.55 (9)	0.24 (9)	0.31 (7)	0.25 (7)
C(9)	0.5107 (3)	0.8395 (3)	0.0876 (1)	1.19 (9)	1.59 (9)	2.27 (9)	−0.13 (7)	0.34 (7)	−0.27 (7)
C(10)	0.6494 (3)	0.7905 (3)	0.0494 (1)	1.11 (9)	2.34 (10)	1.78 (9)	0.02 (7)	0.03 (7)	0.27 (7)
C(1)	0.2902 (3)	0.7288 (3)	−0.0060 (1)	1.42 (10)	2.47 (10)	1.42 (9)	0.19 (8)	0.16 (7)	−0.21 (7)
C(2)	0.1141 (3)	0.7767 (3)	−0.0197 (1)	1.28 (9)	1.35 (8)	1.92 (9)	−0.11 (7)	0.14 (7)	−0.04 (6)
C(3)	0.4069 (3)	0.5831 (3)	0.1112 (1)	1.64 (10)	1.50 (9)	2.11 (10)	0.42 (7)	0.34 (8)	0.03 (7)
C(4)	0.2511 (3)	0.5091 (3)	0.1247 (1)	1.68 (10)	1.43 (9)	2.53 (10)	−0.02 (7)	0.60 (8)	−0.20 (7)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(Cl)	0.294 (4)	0.633 (4)	−0.025 (2)	2.6 (7)	H(C7)	−0.051 (3)	0.577 (3)	0.119 (1)	1.1 (5)
H′(Cl)	0.339 (4)	0.789 (3)	−0.041 (1)	2.1 (6)	H′(C7)	−0.019 (4)	0.496 (3)	0.197 (1)	2.0 (6)
H(C3)	0.458 (3)	0.521 (3)	0.078 (1)	0.7 (4)	H(C9)	0.561 (3)	0.841 (3)	0.138 (1)	1.5 (5)
H′(C3)	0.481 (3)	0.600 (3)	0.157 (1)	0.9 (5)	H′(C9)	0.469 (4)	0.946 (3)	0.070 (1)	2.4 (6)
H(C4)	0.176 (3)	0.501 (3)	0.079 (1)	1.0 (5)	H(O3)	0.839	0.855	0.031	2.3
H′(C4)	0.284 (3)	0.403 (3)	0.149 (1)	1.6 (5)	H(O6)	0.313	1.117	1.141	2.1
H(C5)	0.199 (4)	0.615 (4)	0.293 (2)	3.0 (7)	H′(O6)	0.132	1.113	0.109	2.1
H′(C5)	0.301 (5)	0.506 (4)	0.268 (2)	4.1 (8)					

Experimental Section

Crystals of [Cr($C_9H_{12}N_2O_6$COOH)(H_2O)] (formula weight 359.22) were prepared by the method of Hamm.[6] The crystals are monoclinic with a = 8.370 (5) Å, b = 8.842 (3) Å, c = 17.595 (6) Å, β = 100.05 (3)°, V = 1282.2 Å^3, ρ_{measd} (suspension in dibromobutane–dibromoethane) = 1.84 g cm^{-3}, Z = 4, ρ_{calcd} = 1.86 g cm^{-3}, F(000) = 729, μ(Mo Kα) = 8.54 cm^{-1}, and $P2_1/c$ ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$ (absent)).

Data were collected on a Picker FACS-1 diffractometer using graphite-monochromatized Mo Kα radiation (λ 0.7107 Å). The cell dimensions were calculated from a least-squares program utilizing 13 hand-centered reflections with 2θ between 40 and 50°. Intensity measurements were made by a moving crystal–moving counter technique.[7] There were 13 102 reflections processed by reported methods[8] of which 2814 were unique reflections with $I > 3\sigma(I)$. The 020 reflection is not included in the data set due to overflow of the counter during data collection. Standard reflections (306, 40$\bar{8}$, 080) varied by less than 3% during data collection. No correction for absorption was made, the minimum and maximum transmission factors being 1.17 and 1.20.

The structure of aquo(ethylenediaminetriacetatoacetic acid)chromium(III) was solved with use of standard atomic scattering factors and dispersion corrections.[9] It was assumed that the chromium atom had a charge of positive three and that the other atoms were neutral.[10] Refinement on the hydrogen atoms using isotropic parameters was possible except for H(O3), H(O6), and H′(O6) which are involved in intermolecular hydrogen bonds. Their position parameters were determined from electron density maps, and they were assigned a temperature factor equal to the isotropic temperature factor of the oxygen atom to which they are bound. The refinement converged to final residual values $R_1 = \sum\Delta F/\sum F_o$ = 0.0387 and $R_2 = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$ = 0.0449. Final positional and thermal parameters are given in Table I.

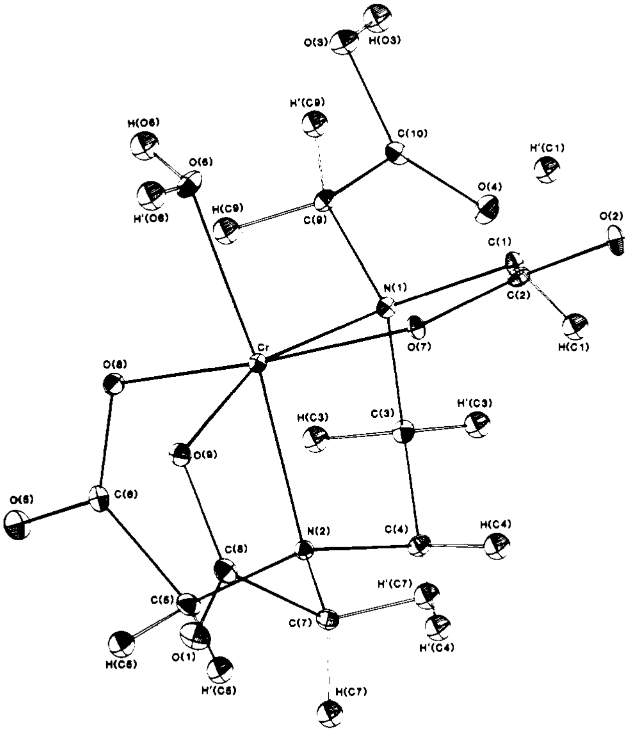

Figure 1. Molecular structure of [Cr(H_2O)HEDTA].

Discussion

Figure 1[11] presents a view of the molecular structure of the title compound. Supplementary Tables I and II list the de-

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Table II. Bond Angles (Deg) and Bond Distances (Å) in [Cr(H_2O)HEDTA] with Standard Deviations

Angles

N(1)–Cr–O(6)	99.31 (10)	C(9)–C(10)–O(3)	108.99 (19)	Cr–N(1)–C(1)	109.44 (11)
N(1)–Cr–O(7)	80.90 (8)	C(9)–C(10)–O(4)	126.50 (22)	Cr–N(1)–C(3)	103.87 (11)
N(1)–Cr–O(8)	91.45 (10)	O(3)–C(10)–O(4)	124.47 (22)	Cr–N(1)–C(9)	108.31 (11)
N(1)–Cr–N(2)	84.78 (9)	C(1)–C(2)–O(2)	119.11 (19)	C(1)–N(1)–C(3)	111.05 (20)
N(1)–Cr–O(9)	162.51 (11)	C(1)–C(2)–O(7)	116.50 (17)	C(1)–N(1)–C(9)	111.20 (21)
N(2)–Cr–O(7)	96.97 (9)	O(2)–C(2)–O(7)	124.39 (19)	C(3)–N(1)–C(9)	112.65 (21)
N(2)–Cr–O(8)	84.57 (8)	C(5)–C(6)–O(5)	120.24 (21)	Cr–N(2)–C(4)	108.60 (11)
N(2)–Cr–O(9)	80.90 (9)	C(5)–C(6)–O(8)	116.00 (18)	Cr–N(2)–C(5)	107.11 (12)
N(2)–Cr–O(6)	172.84 (11)	O(5)–C(6)–O(8)	123.76 (20)	Cr–N(2)–C(7)	105.29 (11)
O(6)–Cr–O(7)	89.51 (8)	C(7)–C(8)–O(1)	120.64 (24)	C(4)–N(2)–C(5)	111.27 (22)
O(6)–Cr–O(8)	89.43 (8)	C(7)–C(8)–O(9)	114.50 (20)	C(4)–N(2)–C(7)	113.81 (21)
O(6)–Cr–O(9)	96.01 (9)	O(1)–C(8)–O(9)	124.83 (20)	C(5)–N(2)–C(7)	110.35 (22)
O(7)–Cr–O(9)	90.89 (10)	⟨X–C–X⟩	119.99	N(1)–C(1)–C(2)	112.60 (17)
O(7)–Cr–O(8)	172.00 (12)			N(1)–C(3)–C(4)	108.84 (18)
O(8)–Cr–O(9)	97.10 (10)			N(1)–C(9)–C(10)	116.28 (18)
Cr–O(7)–C(2)	120.02 (12)			N(2)–C(4)–C(3)	108.30 (19)
Cr–O(8)–C(6)	116.65 (12)			N(2)–C(5)–C(6)	111.84 (18)
Cr–O(9)–C(8)	116.65 (13)			N(2)–C(7)–C(8)	106.92 (19)

Distances

Cr–N(1)	2.141 (2)	N(1)–C(1)	1.497 (3)	C(1)–H(C1)	0.91 (3)
Cr–N(2)	2.041 (2)	N(1)–C(3)	1.515 (3)	C(1)–H′(C1)	0.95 (3)
Cr–O(6)	2.002 (2)	N(1)–C(9)	1.475 (3)	C(3)–H(C3)	0.96 (2)
Cr–O(7)	1.980 (2)	N(2)–C(4)	1.487 (3)	C(3)–H′(C3)	0.94 (2)
Cr–O(8)	1.935 (2)	N(2)–C(5)	1.494 (3)	C(4)–H(C4)	0.94 (2)
Cr–O(9)	1.932 (2)	N(2)–C(7)	1.492 (3)	C(4)–H′(C4)	1.05 (3)
C(1)–C(2)	1.511 (3)	⟨N–C⟩	1.493	C(5)–H(C5)	0.86 (3)
C(3)–C(4)	1.515 (4)	C(2)–O(2)	1.223 (3)	C(5)–H′(C5)	0.89 (4)
C(5)–C(6)	1.510 (4)	C(6)–O(5)	1.228 (3)	C(7)–H(C7)	0.93 (2)
C(7)–C(8)	1.534 (4)	C(8)–O(1)	1.221 (3)	C(7)–H′(C7)	0.93 (3)
C(9)–C(10)	1.503 (3)	⟨C–O$_u$⟩	1.224	C(9)–H(C9)	0.91 (2)
⟨C–C⟩	1.515	C(2)–O(7)	1.299 (3)	C(9)–H′(C9)	1.04 (3)
C(10)–O(3)	1.330 (3)	C(6)–O(8)	1.305 (3)	O(3)–H(O3)	0.96
C(10)–O(4)	1.211 (3)	C(8)–O(9)	1.303 (3)	O(6)–H(O6)	0.95
		⟨C–O$_c$⟩	1.302	O(6)–H′(O6)	0.96

viations of atoms from the least-squares planes around the chromium atom and the angles between these planes. The coordination around the chromium atom is best described as a distorted octahedron. Six intermolecular hydrogen bonds are observed between neighboring molecules in the crystal lattice (supplementary Figure 1[11]). Distances and angles for hydrogen bonds in the crystal lattice are listed in supplementary Table III. This extensive hydrogen bonding is also reported for the Rh(III) structure.[5]

The bond distances given in Table II in comparison to those reported for the Rh(III) complex[5] indicate that respective Cr–N distances are lengthened whereas Cr–O distances are shortened. The bond angles around the Cr(III) atom have an average deviation from 90° of 5.1°. In the structure reports for potassium nitro(ethylenediaminetriacetato)cobalt(III)–1.5-water,[12] (dihydrogen ethylenediaminetetraacetato)aquonickel(III),[13] and the Rh(III) compound[5] the average deviations from 90° are 3.1, 5.5, and 4.0°, respectively. In the nickel complex the large distortion from octahedral geometry is partially explained by an axial distortion toward square-planar geometry.[13] The N–C, C–O, and C–C bond distances and angles listed in Table II are comparable in all of the above structures.

This distortion around the central chromium atom is likely to be present in solution, as large absorptivity coefficients are observed.[3] Chromium(III) complexes are known to undergo associative-type substitution mechanisms, and a catalytic role for the free carboxyl group in [Cr(H_2O)HEDTA] has been suggested.[3] However, even aquo(ethylenediaminetriacetato)chromium(III) and aquo(*N*-methylethylenediaminetriacetato)chromium(III) complexes which lack a free carbonyl group exhibit anation rates 10^1–10^3 times faster than those observed for $[Cr(NH_3)_5H_2O]^{3+}$.[3] The substitution lability of chromium(III) complexes with ground-state distortions has been reported by other workers.[14] Geometrical distortions of the magnitude observed here are also found in metal–peptide complexes. Distortions in Cr–N and Cr–O bond lengths are reported for tris(glycinato)chromium(III) monohydrate,[15] and for sodium bis(L-cysteinato)chromate(III) dihydrate.[16] In the glycine compound the angles around the chromium atom have an average deviation from 90° of 4.4°.[15] A chromium(III) complex of unknown structure is thought to play a unique role in normal glucose metabolism.[17] A substitution-inert complex would appear inappropriate as a biological catalyst, unless of course the metal ion served to define tertiary structure or electrostatic properties. However, given the demonstrated substitution lability of Cr(III)–EDTA complexes[2,3] and the availability of catalytic carboxyl groups in a protein matrix, the role of biological chromium need not be restricted to the latter two functions noted above. Similarity of the proposed carboxyl, amine, and mercaptide binding sites of amino acids in the biological chromium complex[18] with those of EDTA further support this point.

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Registry No. $Cr(H_2O)HEDTA$, 76582-41-7.

Supplementary Material Available: A list of structure factor amplitudes, supplementary Tables I–III (deviations from least-squares planes, angles between least-squares planes, and distances and angles involving hydrogen bonds), and supplementary Figure 1 (unit cell packing and hydrogen bonding in $[Cr(H_2O)HEDTA]$) (15 pages). Ordering information is given on any current masthead page.

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Redetermination of the Crystal Structure of Dimanganese Decacarbonyl and Determination of the Crystal Structure of Dirhenium Decacarbonyl. Revised Values for the Mn–Mn and Re–Re Bond Lengths in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

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While relatively accurate room-temperature X-ray diffraction studies have been carried out on the tetranuclear "binary" carbonyls of the cobalt subgroup ($Co_4(CO)_{12}$,[1] $Rh_4(CO)_{12}$,[2] $Ir_4(CO)_{12}$[3]),on the trinuclear binary carbonyls of the iron subgroup ($Fe_3(CO)_{12}$,[4] $Ru_3(CO)_{12}$,[5] $Os_3(CO)_{12}$[6]) and on the dinuclear species $Fe_2(CO)_9$,[7] there have been no correspondingly accurate studies on the neutral binary carbonyls of the group 7 transition metals.

The species $M_2(CO)_{10}$ (M = Mn,[8] Tc,[9] Re[10]) have previously been shown to be isomorphous. Completed structural studies of $Mn_2(CO)_{10}$[8] and $Tc_2(CO)_{10}$[9] show the molecules to have approximate D_{4d} symmetry. Although there is no question that these structures were correctly determined, each was reported more than 15 years ago, the determination was based on film data and is (by current standards) of limited precision. Thus, the structural study of $Mn_2(CO)_{10}$ was based on 614 visually estimated X-ray diffraction data, and the model was refined to $R_F = 7.0\%$. The resulting Mn–Mn bond length of 2.923 (3) Å has been quoted widely throughout the chemical literature. No complete study of $Re_2(CO)_{10}$ has been reported, although a Re–Re distance of 3.02 Å (from a partial structure)[10] has, again, been quoted frequently.

We now report accurate room-temperature X-ray diffraction studies of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The metal–metal bond lengths thus obtained (along with other geometric features) will be of value in comparison with results from other room-temperature studies of substituted $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ complexes. While a case can be made for carrying out structural studies on this type of molecule only at low temperature (and, in fact, a study of the distribution of bonding electrons in $Mn_2(CO)_{10}$ is currently under way)[11], most structural studies will continue to be carried out under ambient conditions and require comparisons with fundamental structures studied under similar conditions.

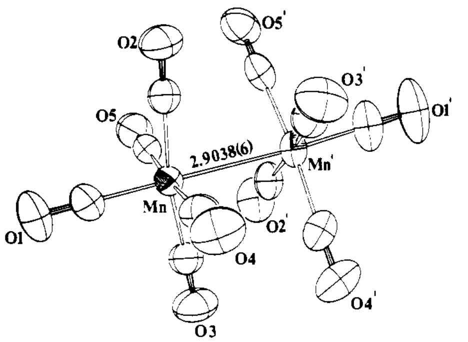

Figure 1. Geometry of the $Mn_2(CO)_{10}$ molecule (ORTEP-II diagram; 30% ellipsoids).

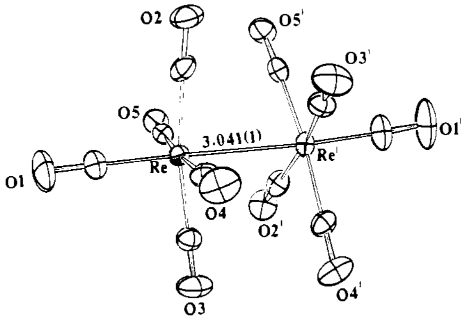

Figure 2. $Re_2(CO)_{10}$ molecule (ORTEP-II diagram; 30% ellipsoids).

Experimental Section

Samples of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from the Strem Chemical Co. An approximately ellipsoidal crystal of $Mn_2(CO)_{10}$ (dimensions 0.23 × 0.30 × 0.30 mm) was obtained from the original sample. Crystals of $Re_2(CO)_{10}$ were grown from a cyclohexane/carbon tetrachloride solution (70:30 v/v); the crystal selected for the X-ray structural study had dimensions of 0.20 × 0.20 × 0.23 mm. Each crystal was sealed into a thin-walled glass capillary under argon and was mounted on a Syntex $P2_1$ automated four-circle diffractometer as described previously;[12] details are presented in Table I.

Two complete asymmetric units of diffraction data were collected for each crystal. Following correction for Lorentz, polarization, and absorption effects, the data were (in each case) merged to a single averaged set. The statistics for averaging ($R(I) = 1.01\%$ for 1260 averaged pairs for $Mn_2(CO)_{10}$ and $R(I) = 2.54\%$ for 1316 averaged pairs for $Re_2(CO)_{10}$) indicate the satisfactory quality of the diffraction data.

Starting with the coordinates of Dahl and Rundle for $Mn_2(CO)_{10}$,[8] full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all atoms (100 parameters vs. 1260 independent reflections) led to final convergence $[(\Delta/\sigma)_{max} < 0.005]$ with $R_F = 2.8\%$, $R_{wF} = 3.7\%$, and GOF = 0.925. The discrepancy indices for those 1107 data with $|F_o| > 3\sigma(|F_o|)$ were $R_F = 2.3\%$ and $R_{wF} = 3.6\%$. The highest feature on a final difference-Fourier synthesis was a peak of height 0.16 e Å^{-3}; tests of the weighting scheme indicated that it was satisfactory and that no correction for secondary extinction was necessary.

The structural analysis of $Re_2(CO)_{10}$ was begun with use of the coordinates obtained in our structure of $Mn_2(CO)_{10}$. Full-matrix least-squares refinement as before (100 parameters vs. 1330 independent reflections) led to final convergence with $R_F = 2.9\%$, $R_{wF} = 2.4\%$, and GOF = 1.203. For those 1207 data with $|F_o| > 3\sigma(|F_o|)$,

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