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Contribution from the Departments of Chemistry and Physics and Astronomy,
Vanderbilt University, Nashville, Tennessee 37235

Reactions of Coordinated Molecules. 22. Crystal and Molecular Structure of $[cis\text{-}(OC)_4Re(CH_3CO)_2]_2Cu$: A Metallaacetylacetonate Complex of Copper(II)

P. GALEN LENHART,*[1a] C. M. LUKEHART,*[1b,c] and L. T. WARFIELD[1b]

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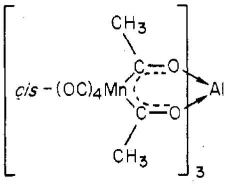
The complex $[cis\text{-}(OC)_4Re(CH_3CO)_2]_2Cu$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.2231$ (9) Å, $b = 7.3648$ (5) Å, $c = 13.9179$ (10) Å, $\beta = 90.791$ (6)°, $V = 1150$ Å^3, $Z = 2$, and ρ(calcd) = 2.403 g cm^{-3} for mol wt 832.22. The molecule has inversion symmetry. Diffraction data (2θ out to 55°) were collected with a four-circle automated Picker diffractometer using Nb and Zr-Y balanced filters and Mo Kα radiation. The structure was refined by using the full-matrix least-squares procedure, and the resulting discrepancy indices were $R = 2.3\%$ and $R_w = 2.6\%$ for 2315 independent reflections. The Cu ion is coordinated to two metallaacetylacetonate ligands where all four Cu–O distances are 1.920 (3) Å. Although the CuO_4 coordination geometry is rigorously planar, the atoms comprising the backbone of each metallaacetylacetonate ligand are not coplanar, resulting in a unique "chaise longue chair" structure for the molecule which preserves the crystallographically imposed inversion symmetry. This molecular structure is distinctly different from the "stepped" structure usually observed for bis-chelate complexes. A long-range interaction between the Cu atom and two of the axial CO ligands of the $Re(CO)_4$ moieties is discussed.

Introduction

The discovery of the metalla-β-diketonate molecules initiated a study of the coordination chemistry and the organic condensation reaction chemistry of these complexes. The elucidation of the molecular structures of these metalla molecules is an important aspect of this continuing investigation.[2]

The structures of two metallaacetylacetonate complexes, **1** and **2**, have been determined previously by X-ray crystallography.[3,4] Complex **1** is a tris(metallaacetylacetonate) complex of Al(III) where the metalla moiety is the *cis*-Mn(CO)$_4$ group, and complex **2** is a neutral, metallaacetylacetone molecule where the metalla moiety is the analogous rhenium fragment. In both complexes the metallaacetylacetonate ligands are structurally similar to the acetylacetonate ligand regarding ligand planarity, intraligand C–O distances, and the O–O "bite" distance.



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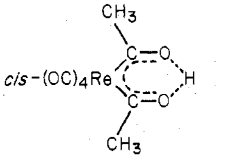

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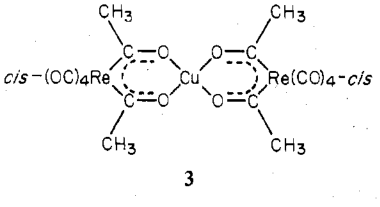
When **2** reacts with anhydrous copper(II) methoxide, the bis(metallaacetylacetonate)copper complex **3** is formed along with the elimination of methanol.[5] Complex **3** is, quite unexpectedly, a deep red solid, and since it represents the first example of a metalla-β-diketonate complex of a transition metal, we wish to report the results of a single-crystal X-ray diffraction study of this complex. The molecular structure of **3** has a distinct "chaise longue chair" appearance and represents the first observation of a nonplanar metalla-β-diketonate ligand. This conformation of the chelate rings places one of the axial carbonyl ligands of each rhenium moiety directly over the two vacant coordination sites of the four-coordinate copper atom. The possibility of a long-range Cu–CO π-bonding interaction is discussed.



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Experimental Section

Collection of X-ray Diffraction Data. Deep red crystals of **3** were prepared by using a literature preparation followed by crystallization from an ether solution at −20 °C.[5] Preliminary precession and cone-axis photographs indicated $2/m$ Laue symmetry and revealed the systematic absences $0k0$ for k odd and $h0l$ for l odd which identified the space group as $P2_1/c$. Cell parameters were determined by a least-squares fit of 2θ, ω, and χ diffractometer settings for 15 reflections in the range $72° < 2\theta < 78°$ as measured at both $\pm 2\theta$ with Cu Kβ radiation ($\lambda = 1.392\,17$ Å). Values for a, b, c, and β, respectively, at 20 °C are 11.2231 (9) Å, 7.3648 (5) Å, 13.9179 (10) Å, and 90.791 (6)°. The calculated volume of the cell is 1150 Å^3. With $Z = 2$ and a molecular weight of 832.22, the calculated density is 2.403 g cm^{-3}.

Intensity data were collected from a freshly grown crystal measuring 0.12 mm × 0.25 mm × 0.50 mm which was mounted with the long axis, b, inclined at about 28° to ϕ on the four-circle automated Picker diffractometer. The control software used for the Picker FACS-I system has been reported previously.[6] All reflections out to 55° in 2θ in the $\pm hkl$ quadrant were measured except for 330 reflections having peak counts of less than 6 counts/s. θ–2θ scans with Nb-filtered Mo Kα radiation were used for reflections with $2\theta > 12°$ and Zr-Y balanced filters for $2\theta < 12°$. Four monitor reflections showed a 4% decline in intensity during the course of 133 h of X-ray exposure. Absorption corrections were calculated for the 2315 reflections with ORABS[7] by use of a linear absorption coefficient of 116.2 cm^{-1} and a Gaussian grid of 9 × 9 × 9. The maximum, minimum, and average transmission factors were 0.3353, 0.0783, and 0.2286, respectively.

Solution and Refinement. A sharpened Patterson function indicated the Re position, which, together with the Cu position (required by symmetry to be on the inversion center), provided the phases for a difference synthesis that revealed the remaining nonhydrogen atoms. After a preliminary full-matrix least-squares refinement with anisotropic thermal parameters, a second calculated difference synthesis revealed a ring of electron density around each methyl carbon position. This result indicated a rotational disorder, and the hydrogen atoms of the disordered methyl groups were approximated by six equally spaced $^1/_2$ hydrogen atoms tetrahedrally located 1.0 Å from the carbon positions. Final refinement of the nonhydrogen parameters was performed by minimizing $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F_o)]^2$. The

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(1) (a) Department of Physics and Astronomy. (b) Department of Chemistry. (c) Research Fellow of the Alfred P. Sloan Foundation (1979–1981).

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Table I. Final Positional and Thermal Parameters[a] (with Esd's) for [*cis*-$(OC)_4Re(CH_3CO)_2]_2Cu$[b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	0.27668 (1)	0.07887 (3)	0.12346 (1)	2.99 (1)	4.11 (1)	3.38 (1)	0.44 (1)	−0.60 (1)	−0.44 (1)
Cu	0	0	0	2.90 (3)	3.61 (3)	3.46 (3)	0.01 (3)	−0.69 (2)	0.33 (3)
O(1)	0.02206 (28)	−0.06665 (40)	0.13195 (21)	3.80 (14)	4.99 (16)	3.82 (13)	−0.76 (12)	−0.60 (11)	0.90 (11)
O(2)	0.06393 (27)	0.23905 (38)	0.01884 (20)	3.98 (14)	3.39 (13)	4.64 (14)	0.10 (12)	−1.12 (12)	0.46 (11)
O(3)	0.49562 (42)	0.28239 (64)	0.03765 (37)	5.47 (23)	9.38 (31)	13.33 (37)	−1.66 (23)	2.43 (24)	0.26 (27)
O(4)	0.42480 (48)	−0.23141 (75)	0.21594 (35)	9.45 (33)	11.64 (37)	10.66 (33)	5.15 (28)	−3.49 (27)	2.27 (28)
O(5)	0.28730 (49)	0.30309 (79)	0.31271 (33)	11.04 (36)	13.34 (39)	7.08 (25)	0.28 (31)	−1.66 (23)	−5.99 (27)
O(6)	0.24927 (36)	−0.14137 (52)	−0.06502 (25)	7.37 (23)	6.25 (20)	4.54 (16)	0.10 (18)	−0.40 (15)	−1.69 (16)
C(1)	0.11467 (43)	−0.04101 (62)	0.17778 (29)	4.46 (22)	4.51 (22)	2.99 (16)	0.09 (18)	−0.30 (15)	0.57 (15)
C(2)	0.15872 (38)	0.27541 (59)	0.06065 (28)	3.30 (18)	3.76 (20)	3.80 (18)	0.05 (16)	−0.24 (15)	−0.15 (16)
C(3)	0.41647 (49)	0.20613 (79)	0.07041 (40)	4.09 (24)	6.33 (32)	6.90 (30)	0.03 (23)	0.21 (22)	−0.66 (25)
C(4)	0.37244 (52)	−0.11658 (87)	0.18187 (41)	5.08 (28)	7.34 (36)	5.67 (27)	1.24 (25)	−1.47 (23)	0.29 (24)
C(5)	0.28285 (51)	0.22444 (86)	0.24372 (39)	5.23 (28)	7.89 (37)	5.44 (26)	−0.11 (26)	−0.98 (22)	−2.33 (26)
C(6)	0.26133 (42)	−0.06276 (58)	0.00365 (34)	3.91 (21)	3.84 (21)	4.27 (20)	0.53 (17)	0.22 (17)	0.23 (17)
C(7)	0.10073 (65)	−0.10098 (95)	0.28147 (36)	8.24 (41)	12.30 (54)	3.62 (23)	−2.08 (36)	−0.82 (24)	3.15 (27)
C(8)	0.18515 (57)	0.47764 (75)	0.06255 (48)	6.75 (33)	3.52 (22)	9.64 (40)	−0.23 (24)	−1.50 (29)	−0.49 (27)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(711)[c]	0.1193	−0.2340	0.2865	11.00	H(811)	0.1423	0.5339	0.1222	11.00
H(721)	0.1564	−0.0316	0.3226	11.00	H(821)	0.2712	0.5006	0.0698	11.00
H(731)	0.0170	−0.0799	0.3036	11.00	H(831)	0.1538	0.5398	0.0054	11.00
H(712)	0.1781	−0.1504	0.3049	11.00	H(812)	0.2244	0.5097	0.1262	11.00
H(722)	0.0758	0.0037	0.3220	11.00	H(822)	0.2359	0.5156	0.0094	11.00
H(732)	0.0387	−0.1988	0.2858	11.00	H(832)	0.1070	0.5489	0.0618	11.00

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Through an oversight, data for this structure were collected and the structure was refined using a unit cell with $\beta = 89.209°$. These atomic parameters correspond to the acute cell. [c] Hydrogen atom positions are denoted by a three-digit number referring to the carbon atom to which the hydrogen atom is bonded and to which set of three tetrahedrally spaced positions it belongs.

Table II. Interatomic Distances in Å (with Esd's) for [*cis*-$(OC)_4Re(CH_3CO)_2]_2Cu$

Cu-Re	3.617 (0)	Re-C(3)	1.963 (6)
Cu-O(1)	1.920 (3)	Re-C(4)	1.978 (6)
Cu-O(2)	1.920 (3)	Re-C(5)	1.990 (6)
C(1)-O(1)	1.241 (6)	Re-C(6)	1.976 (5)
C(2)-O(2)	1.249 (5)	C(3)-O(3)	1.141 (7)
C(1)-C(7)	1.515 (7)	C(4)-O(4)	1.137 (8)
C(2)-C(8)	1.519 (7)	C(5)-O(5)	1.123 (8)
Re-C(1)	2.149 (5)	C(6)-O(6)	1.127 (6)
Re-C(2)	2.155 (4)	O(1)-O(2)	2.783 (4)

variance, σ^2, was based on counting statistics and included the usual instability term (2.5% in this case) as described previously.[8] Atomic scattering factors for the neutral atoms were those tabulated by Cromer and Mann[9] and the anomalous scattering factors for all atoms were those given by Cromer and Liberman.[10] The final R factor was 0.023, and the weighted R factor, R_w, was 0.026 where

$$R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2\}^{1/2}$$

The maximum shift-to-error ratio for the atomic parameters on the final refinement cycle was 0.05 and the standard error of an observation of unit weight was 1.49. The maximum and minimum electron densities on the final difference map were 0.82 and −0.66 e Å^{-3}; both were located near the Re atom. The final positional and thermal parameters are shown in Table I. The values were used before rounding to calculate the final structure factors.

Structure factor, electron density, bond distance and angles, and least-squares calculations were performed with the X-RAY 67 programs[11] as implemented and updated on the Vanderbilt Sigma 7 computer.

Results and Discussion

The crystal structure consists of discrete monomeric molecular units of [*cis*-$(OC)_4Re(CH_3CO)_2]_2Cu$, **3**, which have inversion symmetry. Each Cu atom is on a crystallographic inversion center. The atomic numbering scheme and a view of the molecule from above the coordination plane of the Cu atom are shown in Figure 1. There are no abnormally short intermolecular contacts. The intermolecular H(811)···H(731) distance of 2.217 Å is the shortest such contact, and the four observed H···O(6) distances ranging from 2.512 (4) to 2.756

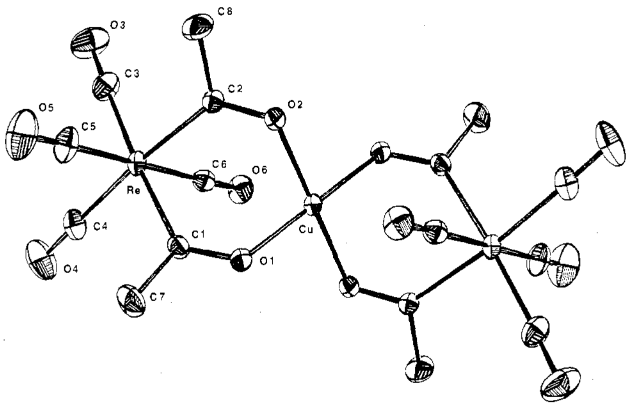

Figure 1. An ORTEP view of **3** (ellipsoids at 20% probability) from above the Cu coordination plane showing the atomic numbering scheme.

Table III. Interatomic Angles (in Deg, with Esd's) for the [*cis*-$(OC)_4Re(CH_3CO)_2]_2Cu$ Molecule[a]

O(1)-Cu-O(2)	92.9 (2)	Re-C(3)-O(3)	178.0 (5)
O(1)-Cu-O(2)′	87.1 (2)	Re-C(4)-O(4)	178.2 (6)
Cu-O(1)-C(1)	124.9 (3)	Re-C(5)-O(5)	178.4 (6)
Cu-O(2)-C(2)	125.6 (3)	Re-C(6)-O(6)	177.9 (6)
O(1)-C(1)-C(7)	111.6 (5)	C(1)-Re-C(4)	91.1 (2)
O(2)-C(2)-C(8)	112.7 (4)	C(2)-Re-C(3)	91.1 (2)
O(1)-C(1)-Re	126.3 (3)	C(3)-Re-C(4)	93.8 (3)
O(2)-C(2)-Re	125.3 (4)	C(5)-Re-C(1)	88.0 (2)
C(1)-Re-C(2)	84.1 (2)	C(5)-Re-C(2)	90.5 (2)
C(1)-Re-C(3)	175.1 (2)	C(5)-Re-C(3)	91.3 (3)
C(2)-Re-C(4)	174.8 (4)	C(5)-Re-C(4)	91.2 (3)
C(5)-Re-C(6)	176.9 (3)	C(6)-Re-C(1)	89.8 (2)
Re-C(1)-C(7)	122.1 (4)	C(6)-Re-C(2)	87.2 (2)
Re-C(2)-C(8)	122.1 (4)	C(6)-Re-C(3)	90.8 (3)
		C(6)-Re-C(4)	91.0 (3)

[a] Primes indicate symmetry-related atoms.

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Table IV. Least-Squares Planes[a] and Atomic Deviations from the Planes

atom	dev, Å	atom	dev, Å
Plane I: $0.9127P - 0.3401Q - 0.2266R = -0.2336 \times 10^{-4}$			
Cu[b]	0	Re	2.269
O(1)[b]	0	C(1)	0.748
O(2)[b]	0	C(2)	0.755
O(1)′[b,c]	0	C(7)	0.447
O(2)′[b,c]	0	C(8)	0.514
		O(6)	3.101
Plane II: $-0.5002P + 0.5615Q + 0.6592R = 0.7995$			
C(1)[b]	0.0011	Re	−0.906
C(2)[b]	−0.0011	Cu	−0.800
O(1)[b]	−0.0011	C(7)	0.773
O(2)[b]	0.0011	C(8)	0.704
Plane III: $0.0733P + 0.5483Q + 0.8331R = 0.1970$			
C(1)[b]	0.0228	Re	0.010
C(2)[b]	−0.0228	Cu	−1.970
C(3)[b]	0.0228	O(1)	−0.689
C(4)[b]	−0.0228	O(2)	−0.733
		C(7)	0.973
		C(8)	0.838
Plane IV: $-0.2148P + 0.5878Q + 0.7800R = 1.2226$			
Re[b]	−0.2131	Cu	−1.223
C(1)[b]	0.2458	C(7)	1.141
C(2)[b]	0.2430	C(8)	1.075
O(1)[b]	−0.1376		
O(2)[b]	−0.1381		
Plane V: $-0.1388P - 0.8337Q + 0.5345R = -0.4113 \times 10^{-5}$			
Cu[b]	0.0000	Re	−0.000
C(5)[b]	−0.0123	O(1)	1.353
O(5)[b]	0.0091	O(2)	−1.428
C(6)[b]	0.0054	C(1)	1.391
O(6)[b]	−0.0021	C(2)	−1.489

[a] The equations of the planes are expressed as $PI + QJ + RK = S$ in orthogonal angstrom space. See text for angles of intersecting planes. [b] Atoms used in calculating the planes. [c] The prime indicates an atom related by inversion.

(4) Å represent normal van der Waals contacts. Interatomic distances and angles are compiled in Tables II and III, respectively, and selected least-squares plane data are listed in Table IV.

The CuO_4 coordination plane is rigorously planar by symmetry. The angle between the plane normal and the *b* axis is 70.12°. The Cu–O(1) and Cu–O(2) distances are 1.920 (3) Å, and the O(1)–O(2) chelate "bite" distance is 2.783 (4) Å. The corresponding Cu–O distances in bis(acetylacetonate)copper, $Cu(acac)_2$, are 1.91 (1) and 1.93 (1) Å with an O–O "bite" distance of 2.82 Å. These values[12] are not significantly different from the corresponding values of **3**. The intra- and interchelate ring angles about the Cu atom of 92.9 (2) and 87.1 (2)°, respectively, indicate a nearly square coordination geometry about the Cu atom of **3**. In $Cu(acac)_2$ these angles are 95.0 and 85.0°.

The two chelate-ring acyl C–O distances are equal within experimental error and have an average value of 1.245 Å. This distance is barely significantly shorter than the average ligand C–O distances in $Cu(acac)_2$ and complex **2** which are 1.29 and 1.27 Å, respectively. The two C(ring)–CH_3 distances of 1.515 (7) and 1.519 (7) Å represent normal C(sp^2)–C(sp^3) single bond distances.

The Re–acyl carbon distances of 2.149 (5) and 2.155 (4) Å are very similar to the average Re–acyl carbon distance (2.16 (2) Å) of **2**. These Re–acyl carbon distances are significantly shorter than the Re to acetyl carbon distance of 2.211 (6) Å observed in *cis*-$(OC)_4Re(CH_3CO)(NH_2Ph)$[13] and may reflect the presence of multiple bonding within the metallaacetylacetonate ligand.

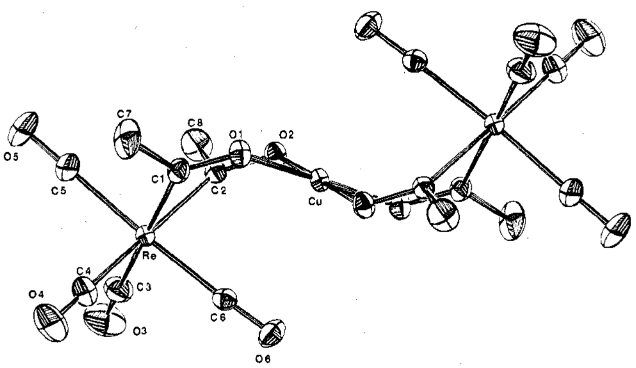

Figure 2. An ORTEP view of **3** (ellipsoids at 20% probability) looking into the copper coordination plane.

The acyl carbon atoms C(1) and C(2) are approximately sp^2 hybridized since the sum of the bond angles about each carbon atom is 360.0°, and the angles centered at each carbon atom have values within the range 120 ± 8°. The intrachelate ring angles of **3** are all within 3° of those angles observed in $Cu(acac)_2$ except for the rhenium-centered angle, C(1)–Re–C(2), of 84.1 (2)°. The corresponding angles in $Cu(acac)_2$ and **2** are 118 (1) and 86.5 (6)°, respectively. As observed in **1** and **2**, the large covalent radius of the metalla atom within the chelate ring affords a sufficiently long metal to acyl carbon distance to compensate for the nearly 90° angle at the metalla moiety.

The coordination geometry about the rhenium atom is approximately octahedral as expected. The average value of the three C–Re–C angles representing the principal coordination axes about the Re atom is 175.6 (3)°. In **3** the axial carbonyl ligands are not significantly tilted toward the metallaacetylacetonate ligand ring as observed in **1** and **2**. The C(5)–Re–C(6) angle in **3** is 176.9 (3)° while the corresponding angles in **1** and **2** are 165.4 (6) and 170.6 (6)°, respectively. This observation would suggest little or no synergistic π bonding in **3** between the axial carbonyl ligands and the metallaacetonate π molecular orbitals.[14] The three-dimensional structure of **3**, which is discussed below, is consistent with this prediction.

While the chelate ring C(1)–Re–C(2) angle is only 84.1 (2)°, the average value for the C–Re–C angles between the remaining adjacent ligands about the Re atom is 90.5 (2)° which indicates approximate octahedral coordination to the Re atom.

The four Re–carbonyl carbon distances are ca. 0.18 Å shorter than the two Re–acyl carbon distances. The difference between the axial and equatorial Re–C distances of 0.012 Å suggests a barely significant trans effect generated by the two acyl ligands. The average values of the C–O distances and the Re–C–O angles within the four terminal carbonyl ligands are 1.132 Å and 178.1°, indicating normal terminally coordinated carbonyl groups.

The unexpected structural feature of **3** is the unusual distortion of the metallaacetylacetonate ligand from planarity. This molecular conformation is shown in Figure 2, and a stereoscopic view of the molecule is shown in Figure 3.

The deviations from planarity within each metallaacetylacetonate ligand and the required inversion symmetry afford a total molecular geometry which resembles a "chaise longue chair" structure. This structure is defined by the following three intersecting planes: plane I [Cu, O(1), O(2), O(1)′, O(2)′]; plane II [C(1), C(2), O(1), O(2)]; and plane III [C(1),

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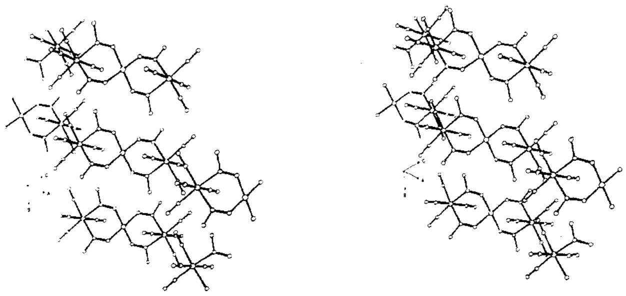
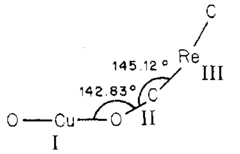


Figure 3. A stereoscopic view of **3** showing molecular packing.

C(2), C(3), C(4)]. The atoms defining planes II and III are coplanar with maximum deviations from these planes of 0.001 and 0.023 Å, respectively. The Re atom lies 0.01 Å from plane III as expected from the pseudooctahedral coordination about this atom.

The dihedral angles between these planes define half of the "chaise longue chair" structure and are shown below.



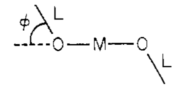
The two dihedral angles are nearly equal, indicating a fairly smooth "curvature" within the molecule, and the total distortion from coplanarity is 72.04° (the acute dihedral angle between planes I and III).

A secondary feature of this chelate ring geometry is that the methyl carbons C(7) and C(8) lie 0.773 and 0.704 Å, respectively, to one side of plane II while the Re atom lies 0.906 Å to the other side of this plane. Molecular models reveal that if the acyl carbon atoms maintain their formal sp^2 geometry, then as the Re atom is displaced from plane II, the methyl groups are displaced concomitantly to the opposite side of the plane. This feature is observed to a much lesser degree in complex **2** where the four acyl C–O atoms are also essentially coplanar (maximum atomic deviation is 0.003 Å). In this complex the Re atom is displaced 0.207 Å to one side of the acyl plane, while the two methyl carbon atoms are displaced 0.263 Å and 0.119 Å to the opposite side of this plane.

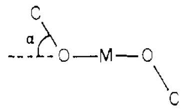
Using the published atomic coordinates reported for $Cr(acac)_2$,[15] we calculate a similar ring distortion for this complex. The four acyl C–O atoms are essentially coplanar (maximum atomic deviation is 0.002 Å), and the central chelate-ring carbon atom lies 0.033 Å to one side of the acyl plane while the two methyl carbon atoms lie 0.018 and 0.089 Å to the other side. Although the distortion within the chelate rings of $Cr(acac)_2$ is similar to that observed for **3**, the magnitudes of the atomic displacements are much less and may be barely significant.

Complex **3** represents the first metalla-β-diketonate complex where the atoms comprising the backbone of the metallachelate ring are not approximately coplanar. In complex **1**, for example, the maximum atomic deviation from the plane defined by the Mn atom, the four chelate-ring acyl C–O atoms, and the two methyl carbon atoms is only 0.096 Å, and the Al atom lies 0.002 Å off of this plane. In complex **2**, the maximum atomic deviation from the plane defined by the Re atom and the two acyl C–O groups is only 0.082 Å. For complex **3**, however, the maximum atomic deviation from the plane defined by Re, C(1), C(2), O(1), and O(2), plane IV, is 0.246 Å, which is nearly three times the observed maximum atomic deviation from similar planes in **1** and **2**.

For planar bis-chelate complexes, the usual structural feature exhibited is the "stepped" structure.[16] This structure occurs when the metal coordination plane and the ligand chelate ring are not coplanar and intersect with an acute dihedral angle, φ, as shown below for an MO_4 planar complex.



For **3** (plane IV), $Cu(acac)_2$, and $Cr(acac)_2$, the values of φ are 55.06, 7.47, and 7.02°, respectively. If only the ligand acyl planes are used, then the acute dihedral angles of intersection with the metal coordination plane, α, drop to 37.17, 4.45, and 6.35°, respectively.



The difference between the values of φ and α for each complex represents the degree of displacement of the central atom within the chelate rings. Clearly, the Re atom in **3** is further removed from the acyl plane than are the central carbon atoms of the acac ligands in $Cu(acac)_2$ and $Cr(acac)_2$. Also, the acyl plane of **3** is 32.7° more inclined to the copper coordination plane than is observed in $Cu(acac)_2$.

The cause of the chelate ring distortion in **3** is uncertain. Although there are four intermolecular H···O(6) interactions of average distance 2.677 Å, it seems unlikely that these interactions would be strong enough to distort the chelate ring so markedly since normal van der Waals O···H distances are in the range of 2.5–2.7 Å.[17]

However, a relatively weak intramolecular interaction might cause this ring bending because the intrachelate ring bond distances of **3** are not significantly different from those observed in **2** where the metallaacetylacetone ligand is planar. The ring distortion in **3** is essentially an angular bending deformation. Also, since the observed chelate-ring bending can be generated from only a slight rotation about the Re–C(1) and Re–C(2) bonds in the free ligand, any dπ–pπ bonding between the Re and acyl carbon atoms will be unaffected by this bending.

A particularly interesting possibility is that the two Re atoms are displaced from the acyl planes so that one of the terminal carbonyl ligands on each Re atom is situated over the Cu atom, thus partially occupying the open coordination sites of the Cu atom. Complex **3** has approximate C_{2h} symmetry (plane V) where the axial carbonyl ligands and the metal atoms are essentially coplanar. This plane nearly bisects the O(1)–Cu–O(2) angle and intersects plane I at 87.9°. The Cu···C(6) and Cu···O(6) distances are 2.970 (5) and 3.108 (4) Å, respectively, and the axial carbonyl ligands C(6)–O(6) and C(6)′–O(6)′ appear to be properly positioned for such an intramolecular bonding interaction with the copper atom.

Such long-range bonding interactions to the metal atoms of planar bis-chelate complexes are not unusual. The metal atoms of $Cu(acac)_2$ and $Cr(acac)_2$ bond intermolecularly to the central carbon atoms of two adjacent acac ligands, thus completing a severely tetragonally distorted octahedral coordination sphere about the metal atoms. The metal to carbon distances which define these weak interactions are 3.01 and 3.048 (5) Å, respectively. The Cu···C(6) and Cu···O(6) distances in **3** are very close to these values and possibly indicate a Cu-to-axial carbonyl ligand interaction in **3**. The copper

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atom in **3** may possess stronger Lewis acidity due to the formal substitution of the electronegative metalla moiety into the backbone of the β-diketonate ligands.

The postulated Cu–axial carbonyl interaction is structurally different from the normal semibridging carbonyl structures so the Re–C(6)–O(6) angle of 177.9 (6)° need not differ significantly from linearity.[18] The average value of the C(6)–Re–C(1) and C(6)–Re–C(2) angles is 88.5 (2)° while the average value of the C(5)–Re–C(1) and C(5)–Re–C(2) angles is 89.2 (2)°. These values may suggest a barely significant (0.7°) increased tilting of the C(6)–axial carbonyl ligand toward the Cu atom. Presumably, the two axial carbonyl ligands would be weakly donating electrons from their π molecular orbitals to the Cu atom, thus acting as formal four-electron ligands. This type of bonding for carbon monoxide has been observed recently for the dimeric molecule $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$.[19] As observed in **3**, the Mo–C–O angles of 175.9 (1.2)° found in this complex are within the normal range expected for linear, terminally coordinated carbonyl ligands and show no excessive bending from linearity even though the carbonyl to metal π bonding within this dimeric complex must surely be greater than that postulated for complex **3**. As expected, the C(5)–O(5) and C(6)–O(6) distances of **3** are not significantly different due to this weak carbonyl–copper interaction.

Another explanation for the nonplanarity of the atoms comprising the backbone of the metallachelate ring is the presence of considerable angle strain within the chelate ring. The sum of the internal angles of a six-membered ring must be 720° if the ring is planar. In complex **1**, the sum of the internal angles of the metallachelate ring is 720°, because the internal angles are able to open up and compensate for the relatively short Mn–acyl carbon distances while maintaining the required geometry and O–O "bite" distance at the Al atom. However, in complex **3**, the sum of the internal angles of the metallachelate ring is only 679°. For this complex these internal angles can not open up sufficiently to compensate for the much longer Re–acyl carbon distances while maintaining the required geometry and O–O "bite" distance at the Cu atom. Additional structural studies should substantiate this effect of internal angle strain.

Recent data may indicate that the "chaise longue chair" structure of **3** persists in the solution phase. The relative intensity pattern for the terminal carbonyl stretching bands of metallaacetylacetonate complexes like **1** and **2** are essentially identical.[20] The assignment of these bands to the particular stretching vibrations of the axial and equatorial sets of carbonyl ligands has been determined.[21] For complex **3**, the relative intensities of the four IR-active carbonyl stretching bands have the expected pattern; however, the axial B_1 band is shifted 17 cm^{-1} to lower energy relative to the equatorial A_1 band. This shift in complex **2** is only 7 cm^{-1}, and the equatorial A_1 bands for **2** and **3** appear at the same frequency. The additional shift in the axial B_1 band of **3** may be caused by the weak coordination of one of the axial carbonyl ligands to the Cu atom. When pyridine is added to a solution of **3**, the axial B_1 band shifts back to its expected position relative to the equatorial A_1 band, apparently, due to the formation of a pyridine adduct which permits a planar conformation of the metallaacetylacetonate ligand. The preparation and characterization of these adducts are currently under investigation.[22]

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Registry No. 3, 67634-87-1.

Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Rutgers, The State University, New Brunswick, New Jersey 08903

Preparation and Structure of Heptakis(*tert*-butyl isocyanide)tungsten(II) Hexatungstate, $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$[1]

WILLIAM A. LARUE, ANH THU LIU, and JOSEPH SAN FILIPPO, JR.*

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The reaction of tripotassium enneachloroditungstate, $K_3W_2Cl_9$, with excess *tert*-butyl isocyanide is promoted by the presence of a small quantity of water and produces the complex heptakis(*tert*-butyl isocyanide)tungsten(II) hexatungstate, $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$. Similar treatment of $Mo_2Cl_9^{3-}$ and $Mo_2Cl_8H^{3-}$ yields the corresponding molybdenum complex ion $(t\text{-}C_4H_9NC)_7Mo^{2+}$. The structure of $[(t\text{-}C_4H_9NC)_7W][W_6O_{19}]$has been determined by single-crystal X-ray diffraction. The compound crystallizes in a monoclinic system. Refinement was performed in group $P2_1/n$ with a = 11.225 (1) Å, b = 33.309 (4) Å, c = 16.852 (3) Å, β = 92.86 (1)°, and Z = 4. The seven-coordinate cation has a coordination geometry which can be described as a distorted monocapped trigonal prism. The structure reveals several similarities and contrasts to that of the corresponding molybdenum cation.

Seven-coordination is becoming a generally recognized occurrence in second- and third-row elements of the early transition metals.[2,3] The electronic and stereochemical principles that govern the selection of such coordination polyhedra as well as the chemical reactivity of these higher

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[1] This work was supported by the National Institutes of Health, Grant AM-18713-03.

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