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Studies on Main Group Metal–Transition Metal Bonded Compounds. 3. Synthesis and Structure of η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ and $[(C_4H_9)_4N][\eta$-$C_5H_5(CO)_3Mo]$

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The crystal and molecular structures of η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ and of $[(n$-$C_4H_9)_4N][\eta$-$C_5H_5(CO)_3Mo]$ have been determined from single-crystal x-ray data collected by counter methods. η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ crystallizes in space group $P2_1/n$ with 4 molecules per unit cell of dimensions a = 11.081 (6) Å, b = 13.115 (10) Å, c = 14.141 (6) Å and β = 102.63 (4)°. Full-matrix least-squares refinements gave discrepancy factors of R_1 = 0.042 and R_2 = 0.049 for 1681 data having $I > 2.5\sigma(I)$. The structure consists of discrete monomers with pseudo-seven-coordinate Mo and Mo–Zn = 2.71 Å, Mo–CO = 2.00 Å, Mo–C_5H_5 = 2.38 Å, Zn–Br = 2.43 Å, and Zn–O = 2.11 Å. $[(C_4H_9)_4N][\eta$-$C_5H_5(CO)_3Mo]$ crystallizes in space group $P2_1/n$ with 4 molecules per unit cell of dimensions a = 9.838 (2) Å, b = 12.568 (3) Å, c = 21.001 (6) Å, and β = 92.11 (2)°. Full-matrix least-squares refinement gave discrepancy factors of R_1 = 0.043 and R_2 = 0.051 for 2133 data having $I > 2.5\sigma(I)$. The structure consists of $(C_4H_9)_4N$ cations and $[\eta$-$C_5H_5(CO)_3Mo]$ anions. The average Mo–CO distance is 1.90 Å and the average Mo–C_5H_5 distance is 2.37 Å. The carbonyl groups of the anion possess pseudo C_{3v} symmetry about an axis passing through the Mo and the center of the ring. The infrared spectra are reported for these molecules and for the $Na[\pi$-$C_5H_5(CO)_3Mo]$ ion pair.

Introduction

We are studying the structures, bonding, and reactivity of compounds which contain direct bonds between a transition metal and a main-group metal. The initial studies in our laboratory have provided the structures and spectroscopic properties of compounds of the classes Tm_2Zn and TmZnX (Tm = η-$C_5H_5(CO)_3M$; M = Mo, W; X = Cl, I).[1] These species included examples of direct Zn–Mo and Zn–W bonds and of a dimeric structure with two chlorine atoms bridging zinc atoms with the fourth coordination site on each zinc atom occupied by a diethyl ether molecule. From the hypochromic shifts in the infrared spectrum, it was inferred that a carbonyl oxygen becomes coordinated to the zinc atom upon loss of ether.

To further elucidate the structures of the transition metal–zinc derivatives in the solid state and to provide a firm basis for discussion of the structures and spectroscopic properties of these materials in solution, an investigation of the zinc bromide and tetra-n-butylammonium derivatives of $[\eta$-$C_5H_5(CO)_3Mo]^-$ is reported. These studies include structural determinations from single-crystal x-ray data and investigation of the infrared spectra of these species. Additional data concerning the behavior of these and related species in solution are reported elsewhere.[2]

Experimental Section

All preparations and subsequent manipulations were carried out under high-vacuum conditions or under an argon atmosphere. Crystals of $[(n$-$C_4H_9)_4N][\eta$-$C_5H_5(CO)_3Mo]$ were prepared by reacting $Na[\eta$-$C_5H_5(CO)_3Mo]$ with $[(n$-$C_4H_9)_4N]Br$ in a 1:3 ratio in a solvent mixture of THF and benzene. Crystals of η-C_5H_5-$(CO)_3MoZnBr\cdot 2THF$ were grown from a 1:1 reaction mixture of $ZnBr_2$ and $[\eta$-$C_5H_5(CO)_3Mo]_2Zn$ in a solvent mixture of THF and hexane. Crystals of both compounds were mounted in capillary tubes under an argon atmosphere and sealed. In addition, the crystals of η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ were mounted with mother liquor present because of their tendency to lose solvent. The crystals were examined on a Syntex $P2_1$ four-circle x-ray diffractometer. Rotation and axial photographs and a small set of counter data were used to determine space groups. Fifteen reflections with 2θ between 12 and 20° for $[(C_4H_9)_4N][\eta$-$C_5H_5(CO)_3MoZn]$ and between 17 and 24° for η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ were centered using a programmed centering routine. Cell constants and errors were obtained by least-squares refinement of these angles. A summary of data collection and crystal parameters for both crystals is given in Table I. The nonconventional space group $P2_1/n$ was used for both crystals so that β would be closer to 90°, thus reducing correlation errors.

Table I. Physical Constants and Experimental Data

	$[(n$-$C_4H_9)_4N]$-$[\eta$-$C_5H_5(CO)_3Mo]$	η-$C_5H_5(CO)_3$-$MoZnBr\cdot 2THF$
Space group	$P2_1/n$	$P2_1/n$
a, A	9.838 (2)	11.081 (6)
b, A	12.568 (3)	13.115 (10)
c, A	21.001 (6)	14.141 (6)
β, deg	92.11 (2)	102.63 (4)
Calcd density, g cm^{-3}	1.133	1.770
Crystal size, mm	0.38 × 0.27 × 0.42	0.38 × 0.30 × 0.30
μ, cm^{-1}	4.993	38.30
2θ scan range (Mo Kα), deg	Kα_1 − 1.0 to Kα_2 + 1.0	Kα_1 − 1.0 to Kα_2 + 1.0
No. of data examined	3722	937 + 1649 = 2586
No. of data with $I > 2.5\sigma(I)$	2133	686 + 995 = 1681
2θ(max), deg	45	45
R_1	0.043	0.042
R_2	0.051	0.049
Max residual electron density, e A^{-3}	0.39	0.28
Error of fit	1.56	1.47
Conventional setting	$P2_1/c$	$P2_1/c$
a, A	9.838	11.081
b, A	12.568	13.115
c, A	22.861	15.945
β, deg	113.36	120.07

Intensity data were collected with Mo Kα radiation which had been diffracted from a highly oriented graphite monochromator whose diffraction vector was parallel to the diffraction vector of the sample. The θ–2θ scan technique was used with a scan rate of 2°/min. Backgrounds were measured at each end of the scan for a total time equal to half the scan time. During data collection, the intensities of three standard reflections were measured every 97 reflections. The standard reflections for $[(C_4H_9)_4N][\eta$-$C_5H_5(CO)_3Mo]$ gave no indication of decomposition or movement. Those for η-C_5H_5-$(CO)_3MoZnBr\cdot 2THF$ decreased just before 0–30° data collection was complete. These data were adequate to determine the gross molecular features. A second crystal was then mounted to obtain data for the 2θ shell between 30 and 45°. This crystal also decomposed in the x-ray beam but provided sufficient data to refine the structure.

For both structures, the data were reduced to I and $\sigma(I)$ by procedures previously described.[3] Standard deviations were assigned as

$$\sigma(I) = [\sigma^2_{\text{counter}} + 0.04I^2]^{1/2}$$

where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I is the net intensity, B is the total

Table II. Atomic Coordinates and Thermal Parameters[a] for $[(n\text{-}C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$ with Estimated Standard Deviations of the Least Significant Figures in Parentheses

	x	y	z		x	y	z
Mo(1)	0.016 37 (7)	0.165 92 (5)	0.337 02 (3)	C(12)	0.0803 (11)	0.3578 (8)	−0.0422 (5)
O(6)	−0.198 2 (7)	0.200 7 (5)	0.228 0 (3)	C(13)	0.4706 (7)	0.1182 (5)	0.0750 (3)
O(7)	0.209 2 (6)	0.312 0 (4)	0.263 8 (3)	C(14)	0.5757 (8)	0.2067 (6)	0.0819 (3)
O(8)	−0.091 9 (6)	0.362 9 (4)	0.405 5 (3)	C(15)	0.6942 (8)	0.1859 (9)	0.0381 (4)
C(1)	0.131 8 (12)	0.000 1 (8)	0.337 5 (5)	C(16)	0.7895 (23)	0.1259 (17)	0.0598 (10)
C(2)	0.177 4 (9)	0.055 6 (8)	0.391 5 (6)	C(16)′	0.8097 (17)	0.2469 (12)	0.0501 (8)
C(3)	0.065 5 (14)	0.069 0 (7)	0.431 0 (4)	C(17)	0.3963 (7)	0.1345 (5)	0.1882 (3)
C(4)	−0.046 1 (10)	0.019 3 (7)	0.402 3 (5)	C(18)	0.4821 (7)	0.0442 (6)	0.2125 (3)
C(5)	−0.006 5 (12)	−0.021 0 (7)	0.344 4 (5)	C(19)	0.5154 (8)	0.0558 (7)	0.2841 (4)
C(6)	−0.118 4 (10)	0.189 1 (6)	0.269 9 (4)	C(20)	0.5940 (11)	−0.0362 (8)	0.3096 (4)
C(7)	0.134 3 (9)	0.257 0 (6)	0.292 0 (4)	C(21)	0.2637 (7)	0.0296 (5)	0.1045 (3)
C(8)	−0.052 4 (7)	0.288 3 (6)	0.378 2 (3)	C(22)	0.1350 (8)	0.0219 (6)	0.1431 (4)
C(9)	0.269 7 (7)	0.229 4 (5)	0.102 3 (3)	C(23)	0.0509 (9)	−0.0751 (8)	0.1199 (4)
C(10)	0.211 2 (8)	0.237 7 (6)	0.034 3 (4)	C(24)	−0.0654 (11)	−0.0995 (9)	0.1618 (5)
C(11)	0.140 7 (9)	0.343 1 (7)	0.025 1 (4)	N(1)	0.3506 (6)	0.1283 (4)	0.1174 (3)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.017 48 (10)	0.006 21 (5)	0.002 28 (2)	0.000 52 (7)	0.000 44 (3)	0.000 43 (3)
O(6)	0.037 4 (14)	0.016 4 (8)	0.005 1 (3)	−0.007 0 (8)	−0.007 6 (5)	0.002 2 (3)
O(7)	0.029 4 (11)	0.008 7 (5)	0.006 0 (2)	0.001 2 (6)	0.007 6 (4)	0.000 5 (3)
O(8)	0.021 7 (9)	0.007 6 (5)	0.003 7 (2)	0.000 8 (5)	0.002 7 (3)	−0.000 1 (2)
C(1)	0.027 2 (20)	0.008 6 (8)	0.003 4 (3)	0.006 4 (10)	0.002 2 (7)	0.001 8 (4)
C(2)	0.019 5 (14)	0.011 4 (10)	0.004 3 (3)	0.003 8 (9)	−0.000 5 (6)	0.002 8 (5)
C(3)	0.033 8 (21)	0.008 3 (8)	0.002 6 (3)	0.002 4 (11)	0.000 4 (7)	0.001 0 (4)
C(4)	0.024 0 (17)	0.007 5 (8)	0.003 7 (3)	0.000 0 (9)	0.002 4 (6)	0.001 7 (4)
C(5)	0.029 0 (20)	0.006 3 (7)	0.004 5 (4)	0.000 3 (9)	−0.001 4 (7)	0.001 5 (4)
C(6)	0.028 2 (16)	0.007 6 (7)	0.003 5 (3)	−0.003 9 (8)	−0.002 7 (5)	0.001 1 (3)
C(7)	0.022 1 (14)	0.007 7 (7)	0.003 1 (2)	0.003 0 (8)	0.003 0 (5)	0.000 2 (3)
C(8)	0.015 5 (11)	0.007 6 (6)	0.002 3 (2)	−0.000 1 (7)	0.001 4 (4)	0.000 5 (3)
C(9)	0.015 0 (11)	0.006 0 (6)	0.003 5 (3)	0.002 3 (7)	−0.000 0 (4)	−0.001 0 (3)
C(10)	0.017 6 (12)	0.007 3 (6)	0.003 6 (3)	0.002 7 (7)	−0.001 1 (4)	−0.000 3 (3)
C(11)	0.027 8 (16)	0.010 2 (8)	0.004 8 (3)	0.006 1 (10)	−0.004 2 (6)	−0.001 5 (5)
C(12)	0.033 1 (19)	0.011 9 (10)	0.006 2 (4)	0.004 4 (11)	−0.004 0 (7)	0.000 8 (5)
C(13)	0.012 0 (10)	0.007 8 (6)	0.002 5 (2)	0.001 4 (6)	0.000 8 (4)	−0.000 8 (3)
C(14)	0.014 6 (11)	0.010 0 (7)	0.003 1 (2)	−0.000 4 (7)	0.000 9 (4)	−0.000 3 (3)
C(15)	0.015 8 (12)	0.018 9 (13)	0.004 3 (3)	0.000 5 (12)	0.000 1 (5)	−0.000 8 (5)
C(16)	($B = 9.0$ (6) Å^2)					
C(16)′	($B = 6.6$ (4) Å^2)					
C(17)	0.012 6 (9)	0.007 5 (6)	0.002 4 (2)	0.000 4 (6)	0.000 4 (3)	−0.001 1 (3)
C(18)	0.017 5 (11)	0.007 8 (6)	0.002 2 (2)	−0.000 9 (7)	−0.000 2 (4)	−0.000 5 (3)
C(19)	0.019 0 (12)	0.011 9 (8)	0.002 9 (2)	0.000 7 (8)	−0.001 0 (4)	−0.000 1 (4)
C(20)	0.036 6 (21)	0.014 4 (10)	0.003 4 (3)	0.000 5 (12)	−0.004 4 (6)	0.000 5 (5)
C(21)	0.015 4 (11)	0.007 2 (6)	0.002 6 (2)	−0.000 8 (6)	0.000 4 (4)	−0.000 9 (3)
C(22)	0.018 7 (3)	0.009 9 (7)	0.003 9 (3)	−0.003 6 (8)	0.000 4 (5)	−0.001 2 (4)
C(23)	0.019 4 (14)	0.017 8 (11)	0.004 7 (3)	−0.007 8 (11)	0.001 0 (6)	−0.001 6 (5)
C(24)	0.030 1 (20)	0.022 1 (14)	0.006 5 (4)	−0.013 4 (14)	0.002 0 (8)	−0.002 9 (6)
N(1)	0.013 2 (8)	0.005 9 (4)	0.002 5 (2)	0.000 1 (5)	0.000 2 (3)	−0.000 8 (2)

[a] The form of the anisotropic thermal parameters for both compounds is $\exp[-(h^2\beta_{12} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; the hydrogen atoms were located 1.0 Å from the attached atom with isotropic thermal parameters (B) set equal to 10% greater than the equivalent B for the attached atom.

background counts, and K is the ratio of scan time to background time. Extinction and absorption corrections were not applied. Data for which $I > 2.5\sigma(I)$ were used in solution and refinement of the structure.[3]

Solution and Refinement of Structures. $[(n\text{-}C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$. The structure was solved by iterative application of the $\sum_2$ relationship using 325 normalized structure factors of magnitude 1.3 or greater. An E map based on the set of phases for the solution with the largest consistency index (0.997) yielded the position of the molybdenum atom. Subsequent Fourier syntheses revealed the remaining nonhydrogen atoms except for the terminal carbon C(16), which was represented as two half-atoms. Inclusion of hydrogen atoms at idealized positions and full matrix refinement with anisotropic thermal parameters on all nonhydrogen atoms except C(16) yielded final discrepancy factors of $R_1 = \sum||F_o| - |F_c||\sum|F_o| = 0.043$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.051$. Table II is a list of atomic coordinates and thermal parameters. Table III contains bond distances and bond angles.

η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$. This structure was also solved by the $\sum_2$ method. The 111 reflections with normalized E's greater than 1.3 were used. The correct set of signs had a consistency index of 0.898. The E map revealed the positions of the Mo, Zn, and Br atoms. Subsequent Fourier syntheses revealed the remaining nonhydrogen atoms and brought the conventional discrepancy factor R_1 for the 0–30° shell to 0.147. Inclusion of the 30–45° data, with a separate scale factor, and idealized hydrogens in a full-matrix refinement with anisotropic thermal parameters on all nonhydrogen atoms yielded discrepancy factors $R_1 = 0.042$ and $R_2 = 0.049$. Table IV is a list of atomic coordinates and thermal parameters. Table V presents bond distances and bond angles. The calculated and observed structure factors for both η-$C_5H_5(CO)_3MoZnBr\cdot 2THF$ and $[(C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$ are available.[9]

Results and Discussion

Structure of $[(n\text{-}C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$. The solid-state structure of $[(n\text{-}C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$ consists of two well-separated ions. The labeling scheme and a projection of the $(CO)_3Mo$ moiety onto the C_5H_5 ring are shown in Figures 1 and 2. A stereoscopic view of the packing arrangement is available.[9]

The anion strongly resembles the isoelectronic η-$C_5H_5(CO)_3Mn$[4] and consists of a molybdenum atom bonded to three carbonyls and to a cyclopentadienyl group. The cyclopentadienyl group is centered above the molybdenum atom with an average Mo–C distance of 2.37 Å. The molybde-

Table III. Interatomic Distances (Å) and Angles (deg) for $[(n\text{-}C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$

Atoms	Distance	Atoms	Angle
Mo-C(1)	2.374 (8)	C(6)-Mo-C(8)	87.9 (3)
Mo-C(2)	2.369 (8)	C(6)-Mo-C(7)	87.8 (4)
Mo-C(3)	2.355 (8)	C(7)-Mo-C(8)	88.5 (3)
Mo-C(4)	2.391 (8)	O(7)-C(7)-Mo	178.7 (7)
Mo-C(5)	2.366 (8)	O(6)-C(6)-Mo	177.8 (9)
Mo-C(6)	1.921 (10)	O(8)-C(8)-Mo	177.5 (7)
Mo-C(7)	1.905 (9)	C(5)-C(1)-C(2)	107.3 (9)
Mo-C(8)	1.901 (8)	C(1)-C(2)-C(3)	107.6 (9)
C(1)-C(2)	1.392 (12)	C(2)-C(3)-C(4)	108.3 (9)
C(2)-C(3)	1.412 (12)	C(3)-C(4)-C(5)	108.3 (9)
C(4)-C(5)	1.382 (11)	C(4)-C(5)-C(1)	109.1 (9)
C(5)-C(1)	1.399 (12)	C(9)-N-C(21)	110.8 (5)
C(6)-O(6)	1.168 (9)	C(9)-N-C(13)	111.1 (5)
C(7)-O(7)	1.185 (8)	C(9)-N-C(17)	106.9 (5)
C(8)-O(8)	1.174 (7)	C(13)-N-C(21)	105.8 (5)
N-C(9)	1.527 (8)	C(13)-N-C(17)	111.6 (5)
N-C(13)	1.511 (8)	C(17)-N-C(21)	110.8 (5)
N-C(17)	1.540 (8)	N-C(9)-C(10)	115.4 (6)
N-C(21)	1.525 (8)	C(9)-C(10)-C(11)	109.7 (7)
C(9)-C(10)	1.524 (10)	C(10)-C(11)-C(12)	112.8 (8)
C(10)-C(11)	1.504 (10)	N-C(13)-C(14)	115.1 (5)
C(11)-C(12)	1.526 (12)	C(13)-C(14)-C(15)	110.3 (7)
C(13)-C(14)	1.522 (9)	C(14)-C(15)-C(16)	116.9 (13)
C(14)-C(15)	1.533 (10)	C(14)-C(15)-C(16)	115.7 (10)
C(15)-C(16)	1.275 (21)	N-C(17)-C(18)	115.7 (5)
C(15)-C(16)′	1.386 (16)	C(17)-C(18)-C(19)	111.1 (6)
C(17)-C(18)	1.493 (9)	C(18)-C(19)-C(20)	111.7 (7)
C(18)-C(19)	1.534 (10)	N-C(21)-C(22)	115.2 (5)
C(19)-C(20)	1.480 (11)	C(21)-C(22)-C(23)	109.0 (7)
C(21)-C(22)	1.532 (10)	C(22)-C(23)-C(24)	112.8 (8)
C(22)-C(23)	1.542 (10)		
C(23)-C(24)	1.500 (12)		

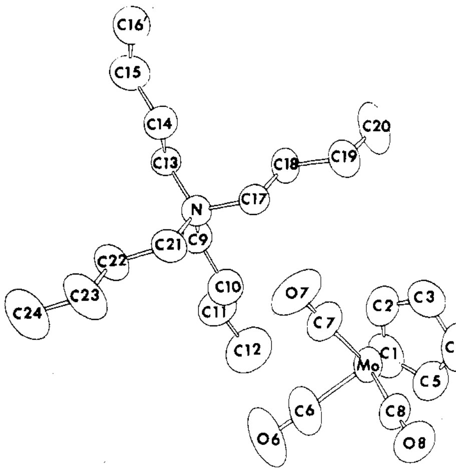


Figure 1. Atomic labeling for $[(C_4H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$.

num–carbonyl distance of 1.90 Å (average) is shorter than reported for other similar structures (Table VI), and the carbonyl C–O distance of 1.18 Å (average) is slightly greater than that observed in other species, suggesting a greater Mo–C bond strength with a concomitant decrease in C–O bonding. Examination of the infrared frequencies associated with the C–O groups (Table VII) clearly reflects this with shifts on the order of 50–60 cm^{-1} toward lower energy.

The plane of the cyclopentadienyl ring is approximately parallel (dihedral angle 3°) to the plane consisting of the three carbonyl carbons. The carbonyl groups possess pseudo $3m\text{-}C_{3v}$ symmetry about an axis passing through the molybdenum and

Table IV. Atomic Coordinates and Thermal Parameters for $\eta\text{-}C_5H_5(CO)_3MoZnBr\cdot 2THF$ with Estimated Standard Deviations of the Least Significant Figures in Parentheses

	x	*y*	*z*		*x*	*y*	*z*
Mo(1)	0.4443 (1)	0.2788 (1)	0.0314 (1)	C(10)	0.9599 (12)	0.1313 (12)	0.0870 (12)
Zn(1)	0.3505 (1)	0.2014 (1)	0.1735 (1)	C(11)	−0.0088 (11)	0.0614 (11)	0.1666 (10)
Br(1)	0.3519 (1)	0.2914 (1)	0.3206 (1)	C(12)	0.1216 (11)	0.0888 (9)	0.2174 (9)
C(1)	0.3076 (11)	0.3594 (8)	0.0600 (8)	C(13)	0.4492 (15)	−0.0239 (9)	0.1774 (11)
C(2)	0.3630 (10)	0.1474 (8)	−0.0082 (8)	C(14)	0.5211 (24)	−0.0960 (13)	0.2475 (17)
C(3)	0.3581 (10)	0.3187 (8)	−0.1023 (8)	C(15)	0.5503 (18)	−0.0500 (13)	0.3430 (16)
C(4)	0.6035 (13)	0.3801 (14)	0.1187 (15)	C(16)	0.4910 (14)	0.0528 (10)	0.3355 (10)
C(5)	0.6124 (11)	0.2831 (17)	0.1599 (9)	O(1)	0.2313 (9)	0.4153 (6)	0.0740 (8)
C(6)	0.6451 (12)	0.2133 (11)	0.0933 (17)	O(2)	0.3162 (8)	0.0714 (6)	−0.0385 (6)
C(7)	0.6481 (11)	0.2688 (14)	0.0103 (10)	O(3)	0.3093 (8)	0.3420 (8)	−0.1769 (7)
C(8)	0.6239 (12)	0.3714 (13)	0.0276 (12)	O(4)	0.1739 (6)	0.1381 (5)	0.1429 (5)
C(9)	0.0803 (10)	0.1617 (11)	0.0587 (9)	O(5)	0.4373 (7)	0.0664 (5)	0.2331 (5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.0067 (1)	0.0058 (1)	0.0054 (1)	−0.0003 (1)	0.0033 (1)	0.000 13 (8)
Zn(1)	0.0082 (1)	0.0054 (1)	0.0056 (1)	0.0001 (1)	0.0037 (1)	−0.000 0 (1)
Br(1)	0.0171 (2)	0.0087 (1)	0.0070 (1)	−0.0012 (1)	0.0055 (1)	−0.002 1 (1)
C(1)	0.0128 (14)	0.0054 (6)	0.0089 (8)	−0.0000 (8)	0.0054 (8)	0.000 7 (6)
C(2)	0.0095 (11)	0.0074 (7)	0.0071 (6)	−0.0008 (7)	0.0055 (7)	−0.001 3 (6)
C(3)	0.0109 (13)	0.0094 (8)	0.0057 (7)	−0.0019 (8)	0.0040 (7)	−0.000 3 (6)
C(4)	0.0088 (15)	0.0148 (15)	0.0144 (15)	−0.0007 (11)	0.0023 (12)	−0.006 5 (13)
C(5)	0.0073 (12)	0.0218 (20)	0.0066 (7)	−0.0003 (13)	0.0023 (7)	0.002 1 (11)
C(6)	0.0076 (14)	0.0097 (10)	0.0209 (19)	0.0009 (9)	0.0017 (13)	0.002 5 (13)
C(7)	0.0078 (12)	0.0156 (15)	0.0101 (9)	−0.0008 (11)	0.0037 (8)	−0.000 8 (10)
C(8)	0.0078 (14)	0.0145 (14)	0.0122 (12)	−0.0053 (11)	0.0022 (10)	0.004 2 (11)
C(9)	0.0064 (12)	0.0147 (12)	0.0091 (8)	−0.0007 (9)	0.0031 (8)	0.003 1 (8)
C(10)	0.0122 (17)	0.0133 (12)	0.0131 (12)	−0.0012 (11)	0.0044 (11)	0.003 3 (10)
C(11)	0.0092 (15)	0.0146 (12)	0.0105 (10)	−0.0016 (10)	0.0069 (9)	0.002 3 (9)
C(12)	0.0130 (15)	0.0107 (9)	0.0087 (8)	−0.0027 (9)	0.0058 (9)	0.001 8 (7)
C(13)	0.0224 (21)	0.0077 (8)	0.0111 (11)	0.0046 (11)	0.0064 (12)	0.000 6 (8)
C(14)	0.0401 (44)	0.0114 (14)	0.0174 (20)	0.0139 (20)	0.0045 (24)	0.002 8 (13)
C(15)	0.0210 (24)	0.0131 (15)	0.0171 (18)	0.0072 (15)	0.0048 (17)	0.005 1 (14)
C(16)	0.0193 (20)	0.0091 (10)	0.0099 (11)	0.0022 (10)	0.0019 (12)	0.003 1 (8)
O(1)	0.0159 (12)	0.0081 (6)	0.0152 (8)	0.0035 (7)	0.0107 (8)	0.001 5 (5)
O(2)	0.0173 (11)	0.0078 (5)	0.0104 (6)	−0.0043 (6)	0.0079 (6)	−0.003 4 (5)
O(3)	0.0142 (11)	0.0167 (9)	0.0073 (9)	−0.0027 (8)	0.0016 (6)	0.001 9 (6)
O(4)	0.0081 (7)	0.0092 (5)	0.0063 (4)	−0.0017 (5)	0.0043 (4)	0.000 6 (4)
O(5)	0.0122 (8)	0.0064 (4)	0.0079 (5)	0.0019 (5)	0.0049 (5)	0.001 3 (4)

Table V. Interatomic Distances (Å) and Angles (deg) for η-$C_5H_5(CO)_3MoZnBr \cdot 2THF$

Atoms	Distance	Atoms	Angle
Mo–C(1)	1.988 (13)	C(1)–Mo–Zn	65.7 (3)
Mo–C(2)	1.974 (10)	C(2)–Mo–Zn	70.2 (3)
Mo–C(3)	2.039 (12)	C(3)–Mo–Zn	129.3 (3)
Mo–C(4)	2.368 (13)	C(1)–Mo–C(2)	100.9 (4)
Mo–C(5)	2.354 (11)	C(1)–Mo–C(3)	80.3 (5)
Mo–C(6)	2.410 (12)	C(2)–Mo–C(3)	81.4 (4)
Mo–C(7)	2.375 (12)	Mo–Zn–Br	123.8 (1)
Mo–C(8)	2.394 (13)	Mo–Zn–O(4)	119.6 (2)
Mo–Zn	2.711 (1)	Mo–Zn–O(5)	113.5 (2)
Zn–Br	2.433 (2)	Mo–C(1)–O(1)	173.7 (9)
Zn–O(4)	2.111 (6)	Mo–C(2)–O(2)	174.8 (10)
Zn–O(5)	2.117 (6)	Mo–C(3)–O(3)	179.2 (12)
C(1)–O(1)	1.181 (13)	C(4)–C(5)–C(6)	107.2 (13)
C(2)–O(2)	1.166 (12)	C(5)–C(6)–C(7)	107.7 (12)
C(3)–O(3)	1.143 (13)	C(7)–C(8)–C(4)	107.3 (14)
O(4)–C(9)	1.464 (13)	C(8)–C(4)–C(5)	108.6 (14)
O(4)–C(12)	1.487 (13)	C(13)–O(5)–C(16)	113.0 (9)
C(9)–C(10)	1.557 (19)	O(5)–C(13)–C(14)	103.8 (13)
C(10)–C(11)	1.454 (19)	C(13)–C(14)–C(15)	111.0 (13)
C(11)–C(12)	1.539 (17)	C(14)–C(15)–C(16)	107.0 (13)
C(4)–C(5)	1.395 (24)	C(15)–C(16)–O(5)	105.1 (13)
C(5)–C(6)	1.435 (23)	C(9)–O(4)–C(12)	111.5 (8)
C(6)–C(7)	1.412 (23)	O(4)–C(9)–C(10)	103.9 (10)
C(7)–C(8)	1.404 (22)	C(9)–C(10)–C(11)	107.1 (11)
C(8)–C(1)	1.395 (24)	C(10)–C(11)–C(12)	106.0 (10)
O(5)–C(13)	1.454 (15)	C(11)–C(12)–O(4)	104.2 (9)
O(5)–C(16)	1.487 (16)		
C(13)–C(14)	1.491 (21)		
C(14)–C(15)	1.480 (27)		
C(15)–C(16)	1.495 (20)		

Table VI. Average Distances (Å) in the η-$C_5H_5(CO)_3Mo$ Moiety

Compd	Mo–C (ring)	Mo–C (carbonyl)	C–O	C–C (ring)	Ref
$[\eta$-$C_5H_5(CO)_3Mo]_2$	2.35	1.96	1.16	1.42	5
η-$C_5H_5(CO)_3MoC_2H_5$	2.38	1.96	1.15	1.43	6
η-$C_5H_5(CO)_3MoCl$	2.36	1.99	1.16	1.36	7
$[\eta$-$C_5H_5(CO)_3Mo]_3Tl$	2.35	1.97	1.15	1.42	8
$[\eta$-$C_5H_5(CO)_3MoZnCl \cdot Et_2O]_2$	2.34	1.95	1.16	1.42	1
η-$C_5H_5(CO)_3MoZnBr \cdot 2THF$	2.38	2.00	1.16	1.42	
$[Bu_4N][\eta$-$C_5H_5(CO)_3Mo]$	2.38	1.90	1.18	1.39	

Table VII. Infrared Carbonyl Stretching Frequencies (cm^{-1}) for selected η-$C_5H_5(CO)_3Mo$ Derivatives

Compd	Freq	Solvent
$Na[\eta$-$C_5H_5(CO)_3Mo]$	1901 s, 1796 s, 1746 s	THF
$[Bu_4N][\eta$-$C_5H_5(CO)_3Mo]$	1896 s, (1786, 1764) b	THF
$Na[\eta$-$C_5H_5(CO)_3Mo]$	1895 s, 1775 b	DMF
η-$C_5H_5(CO)_3Mo_2Zn$	1978 s, 1958 s, 1870 b	THF
η-$C_5H_5(CO)_3MoZnBr$	1964 s, 1879 s, 1849 s	THF
η-$C_5H_5(CO)_3MoZnCl$	1966 s, 1879 s, 1851 s	THF

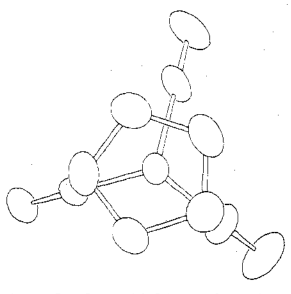


Figure 2. A view of the $[\eta$-$C_5H_5(CO)_3Mo]^-$ anion with the $(CO)_3Mo$ moiety projected onto the C_5H_5 ring with 20% probability thermal ellipsoids.

the center of the cyclopentadienyl ring. This is further illustrated by the appearance of only two IR bands in solution, a band at 1896 cm^{-1} and one broad band with fine structure at 1786 and 1764 cm^{-1}. In contrast, the Na^+ salt of this anion exhibits three IR bands indicating *m*-C_s symmetry; however, in DMF, only two bands appear, indicating that the Na^+ ion has been separated from the transition metal moiety in this strongly polar solvent.

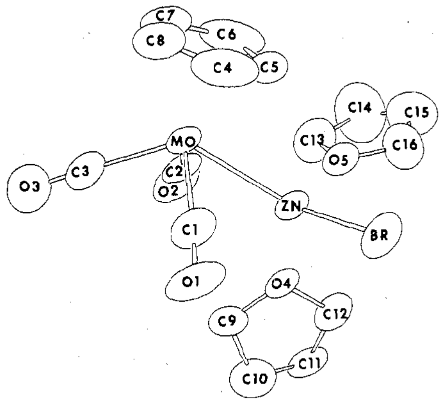


Figure 3. Atomic labeling for η-$C_5H_5(CO)_3MoZnBr \cdot 2THF$.

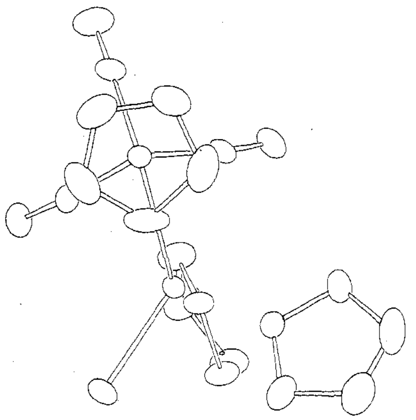


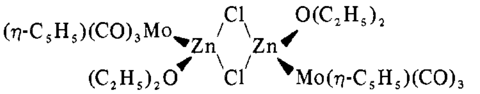
Figure 4. A view of η-$C_5H_5(CO)_3MoZnBr \cdot 2THF$ with the $(CO)_3MoZnBr \cdot 2THF$ groups projected onto the cyclopentadienyl ring with 20% probability thermal ellipsoids.

Structure of η-$C_5H_5(CO)_3MoZnBr \cdot 2C_4H_8O$. The solid-state structure of η-$C_5H_5(CO)_3MoZnBr \cdot 2THF$ consists of discrete monomers. The labeling scheme and a projection of the molecule onto the C_5H_5 ring are shown in Figures 3 and 4, respectively. A stereoscopic view of the packing arrangement is available.[9]

The molybdenum atom is bonded to three carbonyl groups, to a zinc atom, and to a cyclopentadienyl group. The tetrahedral coordination sphere of the zinc is completed by bonds to two tetrahydrofuran oxygen atoms and to a bromine atom. The cyclopentadienyl group is centered above the molybdenum atom with an average Mo–C distance of 2.38 Å, comparable to the structure described above. The Mo–CO distances average 2.00 Å, and the carbonyl C–O distances average 1.16 Å which compare favorably with similar structures (Table VI). The Mo–Zn and Zn–Br distances are 2.71 and 2.43 Å, respectively, and the Zn–O distances average 2.11 Å. The cyclopentadienyl group is approximately parallel (dihedral angle 4°) to the plane consisting of the three carbonyl carbons and the zinc atom.

If one compares the environments of the pseudo-six-coordinate and pseudo-seven-coordinate Mo atoms, one may observe the effect of the addition of the Zn atom to the Mo coordination sphere. The six-coordinate η-$C_5H_5(CO)_3Mo$ moiety is essentially octahedral with the η-C_5H_5 group occupying three coordination sites. The insertion of Zn atom does not affect the coordination of the η-C_5H_5 ring. In order to accomplish this, the Mo–CO bonds elongate by ~0.10 Å and are displaced so as to allow the Zn to occupy a position trans to one carbonyl group.

Comparison of η-$C_5H_5(CO)_3MoZnBr{\cdot}2THF$ with its chloride analogue grown from ether solution shows the difference in coordination ability of diethyl ether and tetrahydrofuran. When the chloride derivative is precipitated from diethyl ether, a dimer forms[1] with bridging chloride ions as indicated in I. The ether molecule occupying the fourth



coordination position of the zinc is easily lost giving rise to the anomalous low-energy infrared band which has been ascribed[1] to Zn←O—C interactions. The present compound which contains bromide ions and THF molecules forms a monomer with two coordination sites on zinc occupied by THF oxygen atoms. The first THF can be removed readily, presumably yielding a molecule analogous to that observed for the chloride with a bridging bromide and a coordinated THF molecule. Removal of the second THF molecule does not occur readily.

Therefore, it appears that the change between the chloride and bromide from dimer to monomer is associated with the increased ability of the THF to coordinate the zinc atom over that of diethyl ether. Thus, the loss of ether gives rise to the formation of the stable dimeric structure observed.

Registry No. $[(n\text{-}C_6H_9)_4N][\eta\text{-}C_5H_5(CO)_3Mo]$, 61618-13-1; η-$C_5H_5(CO)_3MoZnBr{\cdot}2THF$, 61618-14-2.

Supplementary Material Available: Listings of observed and calculated structure amplitudes and stereoscopic views of molecular packing (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **96**, 5427 (1974).
(2) D. E. Crotty and J. P. Oliver, submitted for publication.
(3) (a) Local versions of the following programs were used: SYNCOR, W. Schmonsees' program for data reduction; NEWES, W. Schmonsees' program for generation of normalized structure factors; REL, R. E. Long's program for phase determination by Sayre's method; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP, C. K. Johnson's program for drawing crystal models; HFINDER, A. Zalkin's idealized hydrogen program, modified by T. J. Anderson. (b) Scattering factors for Mo, Zn, Br, O, N, C, and H, including anomalous scattering for Mo, Zn, and Br, were taken from "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974.
(4) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).
(5) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).
(6) M. J. Bennett and R. Mason, *Proc. Chem. Soc., London*, 273 (1963).
(7) S. Chaiwasie and R. H. Fehn, *Acta Crystallogr., Sect. B*, **24**, 525 (1968).
(8) J. Rajaram and J. A. Ibers, *Inorg. Chem.*, **12**, 1313 (1973).
(9) Supplementary material.

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Magnetic Exchange in Transition Metal Dimers. 9. Copper(II) Dimers with Single End-to-End Cyanide Bridges and Unusual Electron Paramagnetic Resonance Spectra

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The preparation of three Cu(II) dimers, $[Cu_2(bpy)_4(CN)](PF_6)_3$ where bpy is 2,2′-bipyridine, $[Cu_2(phen)_4(CN)](PF_6)_3$ where phen is 1,10-phenanthroline, and $[Cu_2(tren)_2(CN)](PF_6)_3$ where tren is 2,2′,2″-triaminotriethylamine, is reported. A single cyanide ion bridges in an end-to-end fashion in each of these compounds. An antiferromagnetic exchange interaction is present in each dimer, as evidenced by variable-temperature (4.2–267 K) magnetic susceptibility data. Exchange parameters (J) are found to be −9.4, −29, and −88 cm^{-1}, respectively, by least-squares fitting to the spin Hamiltonian, $\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$. Essentially isotropic signals at $g \simeq 2.1$ are seen in the X-band and Q-band EPR spectra of all three compounds with the exception of the Q-band spectrum of the bipyridine compound where signals at $g = 2.165$ and 2.118 are seen. The local Cu(II) ion environments are most probably trigonal bipyramidal in these three dissimilar ion dimers and the isotropic signals are shown to result from an *intradimer* electron exchange that averages the **g** tensors of the two different Cu(II) ions.

Introduction

Cyanide ions are known to bridge in an end-to-end fashion between transition metal ions in polymeric and dimeric complexes.[2–6] As recent as 1971, the first x-ray structure of a dimeric complex with a single end-to-end cyanide bridge was reported[7] for $(NC)_5Co\text{-}CN\text{-}Co(NH_3)_5{\cdot}H_2O$. A few years later, the x-ray structure and the presence of an antiferromagnetic exchange interaction were reported for $[Cu_2([14]4,11\text{-diene-}N_4)_2(CN)](ClO_4)_3$, where [14]4,11-diene-$N_4$ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.[8] The local copper atom environments in the dimeric cation were found to be distorted trigonal bipyramids. The $J = -4.8$ cm^{-1} exchange interaction is effected by the cyanide ion bridging from an equatorial site on one Cu(II) ion to an equatorial site on the second Cu(II) ion.

In this paper, we report the preparation of three new dimeric Cu(II) complexes that also are bridged by a single cyanide ion in an end-to-end fashion. The three complexes were prepared, on the one hand, to further investigate magnetic exchange interactions between Cu(II) ions as propagated by cyanide ions. It was of interest to see how large the antiferromagnetic interaction could become with this bridge. More importantly, we were interested in such Cu–CN–Cu complexes because they are examples of rarely encountered paramagnetic dimers in which the two metal ions are in slightly different environments. In a cyanide-bridged copper dimer, obviously, one Cu(II) ion is bonded to the nitrogen atom and the other to the carbon atom of the cyanide ion. In such dissimilar-ion dimers, an increase in the exchange interaction from a negligible J value (relative to the difference in g values) to an appreciable J value results in dramatic changes in the EPR spectra of the complexes as a consequence of the increasing frequency at which electrons exchange between the two Cu(II) ions.

Experimental Section

Compound Preparation. Samples of $[Cu_2(phen)_4(CN)](PF_6)_3$ were prepared in the following way. In 200 mL of distilled water were dissolved 0.24 g of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.40 g of 1,10-phenanthroline. Dilute nitric acid was added to adjust the pH of the solution to 1.75. An aqueous solution of 0.15 g of NaCN (sixfold stoichiometric excess)