Table I. $^{13}C^a$ and $^{55}Mn^b$ Data for $(RNC)_6MnBF_4$ in CD_3CN at Room Temperature

R	$^1J(^{55}Mn-^{13}C)$, Hz	multiplet width,^{c} Hz	^{55}Mn NMR line width,^{d} Hz
methyl	121	581	28.9
ethyl	119	577	33.4
isopropyl	118	561	36.7
tert-butyl	113	540	40.7
cyclohexyl	111	523	42.9

[a] ^{13}C data were obtained with a Nicolet NT200WB instrument on saturated solutions at 50.31 MHz with a 6-μs pulse width and a 750-ms postacquisition delay. Typically, 20 000-30 000 scans were collected in double precision in a 64K block size. [b] ^{55}Mn data were obtained with the Nicolet instrument at 49.52 MHz with a 20-μs pulse width and 500-ms post-acquisition delay in a 16K block size on 0.02 M solutions. Typically, 2000-10 000 scans were obtained. [c] Separation between the outer two peaks of the six-peak multiplet. [d] Widths are at half-height, obtained by fitting the frequency domain data to a Lorentzian line shape by using a least-squares minimizing program available on the Nicolet instrument.

lattice relaxation time (T_1) of the quadrupolar nucleus is long compared to the inverse of the coupling constant (J). When T_1 is comparable to $1/J$, the line shape becomes more complex. Suzuki and Kubo[12] have calculated a series of NMR line shapes for such a case as a function of T_1 and J. The general trend is that as T_1 decreases, the total width of the multiplet decreases and the lines acquire different widths. This narrowing continues until the individual components of the multiplet become unresolvable and a broad absorbance results. When T_1 is much shorter than $1/J$, the signal becomes a sharp singlet. The $(RNC)_6MnBF_4$ system seems to be in the intermediate region bordering on the long T_1 side.

When T_1 is long compared to $1/J$, $^1J(^{55}Mn-^{13}C)$ can be obtained from measuring the peak separation within the multiplet. When T_1 is in the intermediate range described above, the coupling constant is best obtained by comparing the experimental spectra to computer-simulated spectra calculated with varying T_1 and J.[12,13,14] Such a procedure requires a better signal-to-noise ratio than we have been able to obtain. Our estimate of $^1J(^{55}Mn-^{13}C)$ comes from the separation of the center two peaks of the multiplet. The values obtained in this manner will be close to the actual values.

Table I shows that the width of the ^{55}Mn line increases with increasing size of the R group. Assuming that the system is in the "extreme narrowing" region (i.e. $T_1 = T_2$), then as R increases in size, T_1 of Mn decreases. This leads to a decrease in the width of the ^{13}C multiplet with increasing R group size, as observed here and predicted for such a case by Suzuki and Kubo.[12] The decrease in T_1 for ^{55}Mn with increasing size of the R group probably originates in increased deviations from octahedral symmetry due to collisions and intramolecular motions in the larger, more flexible complexes. This distortion produces electric field gradients and hence increases the relaxation rate due to quadrupolar interactions. The decrease in T_1 with the larger molecules can also be explained by the fact that T_1 is inversely proportional to the correlation time, which in turn is proportional to the volume of the molecule. Larger molecules with larger volumes increase the correlation time and decrease T_1.[15]

The coupling constant values reported here should be of interest to both experimentalists and theoreticians. There are reports of ^{13}C NMR studies on organometallic complexes of manganese where the authors failed to observe the NMR peak due to the carbon bonded to manganese.[16] Our results show that the signal is observable and characteristic, at least in symmetric complexes. Theoretical calculations of coupling constants continue to be of interest. The experimental values reported here (Table I) should provide a test of these theories. Mann[17] calculated $^1J(^{55}Mn-^{13}C)$ for $Mn(CO)_6^+$ using a very simplified theory and obtained a value of 110 Hz. This value compares well with those reported in this work.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 824102. The Boeing Co. contributed through partial funding to the purchase of the Nicolet NMR spectrometer. We are grateful for the assistance of Don Appel in obtaining the NMR measurements.

Registry No. $(RNC)_6MnBF_4$ (R = methyl), 91281-18-4; $(CH_3CH_2NC)_6MnBF_4$, 91281-19-5; $(RNC)_6MnBF_4$ (R = isopropyl), 91281-21-9; $(RNC)_6MnBF_4$ (R = *tert*-butyl), 91281-22-0; $(RNC)_6MnBF_4$ (R = cyclohexyl), 89463-46-7; ^{13}C, 14762-74-4.

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Copper(I) and Copper(II) Complexes of 3-Methoxy-1,5-dithiacyclooctane. Evidence of a Long-Range Electrostatic Interaction in the Copper(I) Complex Giving an "Apparent" Five-Coordinated Complex

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The eight-membered mesocyclic dithioether 1,5-dithiacyclooctane (1,5-DTCO) rapidly reduces $Cu(ClO_4)_2$ to $Cu(1,5\text{-}DTCO)_2ClO_4$ such that no Cu(II) complexes have been isolated.[1] Substitution of a hydroxyl group at the three-position of the ring (3-hydroxy-1,5-dithiacyclooctane, 3-OH-1,5-DTCO) gives a ligand that completely inhibits the reduction of Cu(II).[1] However, when the three-position is substituted by a methoxyl group (3-methoxy-1,5-dithiacyclooctane, 3-OMe-1,5-DTCO), both Cu(I) and Cu(II) complexes can be isolated and characterized. This tridentate ligand is one of few ligands that give cationic complexes with both Cu(I) and Cu(II) in which no additional ligands (solvent or anions) are involved in coordination. The structure of the Cu(I) complex is unusual in that one of the methoxyl oxygen atoms is situated in a potential energy well that imparts an "apparent" five-coordinated trigonal-bipyramidal geometry to Cu(I).

Experimental Section

Preparation of Compounds. Reagents. The following reagents were obtained from the indicated sources: 3-hydroxy-1,5-dithiacyclooctane (1,5-dithiacyclooctan-3-ol) from Aldrich Chemical Co., Milwaukee, WI; $Cu(ClO_4)_2\cdot 6H_2O$ from G. Frederick Smith Chemical Co., Columbus, OH.

3-Methoxy-1,5-dithiacyclooctane. A reflux condenser, an addition funnel, and a nitrogen inlet were placed on a 300-mL, three-necked, mortonized, round-bottom flask. A 50% dispersion of sodium hydride in oil (4.80 g, 100 mmol) was washed with pentane to give a gray powder. A magnetic stir bar, tetrahydrofuran (60 mL), and the washed

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[1] Musker, W. K.; Olmstead, M. M.; Kessler, R. M. *Inorg. Chem.* **1984**, *23*, 1764-1768.

sodium hydride were added to the reaction flask. The flask was purged with nitrogen, and methyl iodide (17.0 g, 120 mmol) was added. A solution of 3-hydroxy-1,5-dithiacyclooctane (9.86 g, 60.0 mmol) in tetrahydrofuran (25 mL) was added dropwise to the reaction mixture over a 30-min period. The reaction mixture was refluxed for 30 min and cooled to room temperature. The reaction mixture separated into two layers; the organic layer was washed with saturated solutions of sodium chloride and dried over anhydrous sodium sulfate. The solvent was removed from the dried organic layer by rotoevaporation to give a yellow oil. Pentane-washed sodium hydride (0.125 g, 5.21 mmol) was added to the oil with the evolution of gas, and the mixture was distilled (93–95 °C (0.035 torr)) to give 5.58 g (52.2% yield) of a pale yellow liquid.

Anal. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91. Found: C, 47.55; H, 7.85.

^1H NMR ($CDCl_3/Me_4Si$): δ 2.15 (m, 2 H, CCH_2C), 2.74 (t, 4 H, SCH_2C), 2.98 (d, 4 H, SCH_2C), 3.33 (s, 3 H, OCH_3), 3.47 (m, 1 H, tertiary proton).

Cu(3-OMe-1,5-DTCO)$_2$(ClO$_4$)$_2$. A 14-mL portion of a 0.100 M methanol solution of 3-OMe-1,5-DTCO was added to a 7-mL portion of a 0.100 M methanol solution of $Cu(ClO_4)_2$. The mixture turned dark immediately, and precipitation occurred after a few minutes. The mixture was placed at −5 °C overnight and filtered. The crystals consisted of a mixture of dark purple microneedles and *very* light purple microneedles. The two different crystals were separated manually to give 0.22 g (44% yield) of dark purple crystals.

Cu(3-OMe-1,5-DTCO)$_2$ClO$_4$. Method 1. A 14-mL portion of a 0.100 M methanol solution of 3-OMe-1,5-DTCO was added to a 3.5-mL portion of a 0.100 M methanol solution of $Cu(ClO_4)_2$. The solution was refluxed on a steam bath for 24 h, and the volume was reduced to 100 mL. The solution was cooled at −5 °C overnight and filtered. The solid was recrystallized from hot methanol to give 82 mg (1.6×10^{-4} mol) of colorless crystals, 45% yield.

Method 2. A 0.100 M solution of 0.250 g of Cu(3-OMe-1,5-DTCO)$_2$(ClO$_4$)$_2$ in 4 mL of methanol was prepared. Hypophosphorus acid was added dropwise until the solution became clear. The solution was evaporated at room temperature and atmospheric pressure to give oily, colorless crystals. The crystals were recrystallized from hot methanol; yield 67 mg (32%).

X-ray Crystallography

Cu(3-MeO-1,5-DTCO)$_2$ClO$_4$·CH$_3$OH. Crystals suitable for data collection were obtained from the methanolic reaction mixture. A well-formed crystal was selected and mounted with its long dimension parallel to ϕ in the $N_2(g)$ cold stream of a P2$_1$ diffractometer. Determination of the space group, $Pna2_1$ (No. 33), followed from the conditions $0kl$ ($k + l = 2n$) and $h0l$ ($h = 2n$). A 1.5% decay in the intensity of two standard reflections occurred during the period of data collection. The data were scaled to adjust for this determination. In addition, an empirical absorption correction[2] and Lorentz and polarization corrections were applied. Scattering factors and corrections for anomalous dispersion were from common sources.[3]

The structure was solved by solution of the Patterson map and computation of a difference map. Refinement of non-hydrogen atoms using isotropic thermal parameters converged at $R = 0.076$. Hydrogen atoms were located on a subsequent difference map. The x, y, z coordinates of the hydroxyl hydrogen were refined while U_{iso} was held fixed at 0.04 Å^2. The parameters of the remaining hydrogen atoms were refined by using a riding model with C–H distances of 0.96 Å and $U_{iso} = 1.2U_{iso}$ of the bonded carbon. The original choice of hand was verified by refining to 1.0 (2) a parameter that multiplies all $\Delta f''$ values".[2] Final refinement was carried out with anisotropic thermal parameters assigned to Cu, S, and O atoms. The weighting scheme was $[\sigma^2(F) + 0.0009F^2]^{-1}$. Two peaks in the final difference map were approximately the size of a hydrogen atom (1.41 and 1.22 e Å^{-3}) but were judged to be spurious. Crystal data and data collection parameters are summarized in Table I. Final positional parameters are given in Table II. Selected bond distances and angles can be found in Table III. Complete listings of distances and angles, hydrogen atom coordinates, anisotropic thermal parameters, and structure

Table I. Crystal Data for Bis(3-methoxy-1,5-dithiacyclooctane)-copper(I) Perchlorate Methanol Solvate and Bis(3-methoxy-1,5-dithiacyclooctane)copper(II) Perchlorate

	Cu^I(3-MeO-1,5-DTCO)$_2$ClO$_4$·CH$_3$OH	Cu^{II}(3-MeO-1,5-DTCO)$_2$(ClO$_4$)$_2$
formula	$CuC_{15}H_{32}ClO_6S_4$	$CuC_{14}H_{28}Cl_2O_{10}S_4$
fw	551.67	619.08
color and habit	colorless parallelepipeds	purple needles
space group	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)
a, Å	14.987 (4)	6.699 (1)
b, Å	19.483 (4)	9.391 (1)
c, Å	7.563 (2)	9.741 (1)
α, deg		67.73 (1)
β, deg		79.03 (1)
γ, deg		87.02 (1)
T, K	140	140
Z	4	1
cryst dimens, mm	0.12 × 0.25 × 0.37	0.06 × 0.14 × 0.65
d_{calcd}(140 K), g cm^{-3}	1.66	1.85
d_{measd}(298 K), g cm^{-3}	1.65	1.79
radiation	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	15.0	16.3
range abs cor factors	1.02–1.42	1.09–1.22
diffractometer	P2$_1$	P2$_1$
scan method	ω	ω
2θ range, deg	0–55	0–50
hkl	0 to 20,0 to 26,0 to 10	0 to 8, −11 to 11, −11 to 11
scan speed, deg min^{-1}	15	8
no. of unique data	2730	1953
no. of unique obsd data ($I > 2\sigma(I)$)	2339	1714
no. of parameters refined	181	142
R^a	0.052	0.025
$R_w{}^b$	0.052	0.028

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$.

Table II. Coordinates of Refined Atoms (×10^4) for Cu^I(3-MeO-1,5-DTCO)$_2$ClO$_4$·CH$_3$OH

atom	x	y	z
Cu	7347 (1)	6 (1)	7187 (2)
Cl	213 (1)	1910 (1)	1900 (3)
S(1)	7181 (1)	621 (1)	9817 (4)
S(2)	8780 (1)	394 (1)	6725 (3)
S(3)	6237 (1)	48 (1)	5101 (3)
S(4)	7197 (1)	−1181 (1)	7666 (3)
O(1)	7231 (3)	1531 (3)	6193 (7)
O(2)	7439 (3)	−1443 (2)	2324 (8)
O(3)	538 (4)	1346 (3)	884 (8)
O(4)	−641 (3)	2124 (3)	1238 (10)
O(5)	836 (3)	2471 (3)	1785 (11)
O(6)	113 (5)	1689 (4)	3702 (9)
O(7)	5369 (3)	1395 (3)	7060 (10)
C(1)	7437 (5)	1507 (4)	9301 (11)
C(2)	7880 (4)	1662 (4)	7541 (10)
C(3)	8782 (4)	1321 (3)	7171 (11)
C(4)	9347 (5)	66 (4)	8687 (12)
C(5)	8840 (9)	−98 (6)	10244 (22)
C(6)	8239 (7)	376 (5)	11062 (16)
C(7)	7475 (6)	1775 (4)	4475 (13)
C(8)	6487 (5)	−625 (3)	3506 (10)
C(9)	7302 (4)	−1078 (3)	3931 (10)
C(10)	7215 (4)	−1576 (3)	5484 (10)
C(11)	6011 (5)	−1254 (4)	8277 (11)
C(12)	5316 (4)	−1044 (3)	6901 (12)
C(13)	5290 (5)	−294 (4)	6330 (11)
C(14)	8326 (4)	−1719 (3)	2144 (12)
C(15)	4978 (5)	4978 (5)	7964 (13)
H	5884 (50)	1402 (39)	6879 (136)

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(2) The absorption correction program and others employed were part of the SHELXTL, version 3 (July 1981) package by G. M. Sheldrick installed on a Data General Eclipse computer.

(3) "International Tables for x-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. Distances (Å) and Angles (deg) in the Coordination Sphere for $Cu^I(3\text{-MeO-1,5-DTCO})_2ClO_4{\cdot}CH_3OH$

Distances			
Cu–S(1)	2.335 (3)	Cu–S(4)	2.351 (2)
Cu–S(2)	2.304 (2)	Cu···O(1)	3.069 (5)
Cu–S(3)	2.294 (3)	O(1)···H	2.10 (8)
Angles			
S(1)–Cu–S(2)	93.4 (1)	S(3)–Cu–S(4)	94.1 (1)
S(1)–Cu–S(3)	119.3 (1)	S(1)–Cu···O(1)	72.9 (2)
S(1)–Cu–S(4)	111.3 (1)	S(2)–Cu···O(1)	72.4 (2)
S(2)–Cu–S(3)	124.0 (1)	S(3)–Cu···O(1)	75.9 (2)
S(2)–Cu–S(4)	115.8 (1)	S(4)–Cu···O(1)	169.8 (2)
C(2)–O(1)–C(7)	114.4 (6)	Cu···O(1)···H	83 (3)
Cu···O(1)–C(2)	87.7 (1)	C(2)–O(1)···H	120 (6)
Cu···O(1)–C(7)	121.9 (1)	C(7)–O(1)···H	121 (6)

Table IV. Coordinates (×10⁴) for $Cu^{II}(3\text{-MeO-1,5-DTCO})_2(ClO_4)_2$

atom	*x*	*y*	*z*
Cu	0	10000	0
Cl	13897 (1)	7056 (1)	6761 (1)
S(1)	2919 (1)	8735 (1)	818 (1)
S(2)	−1995 (1)	8442 (1)	2283 (1)
O(1)	469 (3)	11308 (2)	1574 (2)
O(2)	13384 (3)	6013 (2)	8311 (2)
O(3)	15407 (3)	6367 (2)	5955 (2)
O(4)	12107 (3)	7341 (2)	6087 (2)
O(5)	14680 (3)	8481 (2)	6687 (3)
C(1)	2881 (4)	9279 (3)	2427 (3)
C(2)	945 (4)	10054 (3)	2867 (3)
C(3)	−984 (4)	9058 (3)	3582 (3)
C(4)	−1324 (4)	6429 (3)	2849 (3)
C(5)	845 (4)	6021 (3)	3038 (3)
C(6)	2472 (4)	6661 (3)	1624 (3)
C(7)	1664 (4)	12683 (3)	1167 (3)

Table V. Selected Bond Distances (Å) and Angles (deg) for $Cu(3\text{-MeO-1,5-DTCO})_2(ClO_4)_2$

Distances			
Cu–S(1)	2.346 (1)	Cu–S(2)	2.340 (1)
Cu–O(1)	2.369 (2)		
Angles			
S(1)–Cu–S(2)	89.9 (1)	S(2)–Cu–S(1′)	90.1 (1)
S(1)–Cu–O(1)	81.9 (1)	S(2)–Cu–O(1)	79.5

factor amplitudes are available as supplementary material.

$Cu(3\text{-MeO-1,5-DTCO})_2(ClO_4)_2$. A well-formed, purple needle of this complex was obtained from a methanol solution to which one drop of ethylene glycol had been added to prevent adhesion of the crystals to the sides of the flask. The procedure for data collection and reduction was the same as above except that no decay in two standard reflections was noted. Since the density measurement indicated $Z = 1$, the complex was expected to have a center of symmetry, and the Cu atom was placed at (0,1,0). The sulfur and chlorine atoms were located on a Fourier map, and the remaining atoms were found after a few cycles of refinement and computation of a difference map. Refinement proceeded smoothly, with anisotropic thermal parameters assigned to all non-hydrogen atoms in the final cycles. The weighting scheme was $[\sigma^2(F) + 0.0003F^2]^{-1}$. Maximum and minimum peak heights on the final difference map were 0.34 and −0.62 e Å^{-3}, respectively. Crystal data and data collection parameters are given in Table I. Positional parameters are in Table IV; selected bond distances and angles are in Table V. Complete listings of distances and angles, calculated hydrogen atom coordinates, anisotropic thermal parameters, and structure factor amplitudes are available as supplementary material.

Description of the Structures of the Complexes

$Cu(3\text{-OMe-1,5-DTCO})_2(ClO_4)_2$. The crystal structure of $Cu(3\text{-OMe-1,5-DTCO})_2(ClO_4)_2$ consists of centrosymmetric cations as depicted in Figure 1. As seen in the drawing the Cu(II) has a donor set of S_4O_2. The four thioether sulfur atoms constitute a plane, with the two oxygen atoms tilted 10.5° off a vertical to the plane at the Cu(II) center. This distortion can be attributed to the constraints imposed by the tricoordinated ligand. Nevertheless, the overall geometry of Cu(II) can be considered as tetragonal with Cu(II)–S distances of 2.340 and 2.346 Å and a Cu(II)–O bond distance of 2.369 (2) Å. The Cu(II)–S distances are normal. The Cu(II)–O distance is comparable to the few reported for complexes with weakly coordinating alcohols, but we are not aware of any for ethers. The semicoordinated alcohols have distances ranging from 2.341 (3) to 2.528 (9) Å.[4–7] The similarity between alcohol and ether coordination is borne out by the close agreement between the Cu(II)–OMe distance of 2.369 (2) Å in $Cu(3\text{-OMe-1,5-DTCO})_2(ClO_4)_2$ and the Cu(II)–OH distance of 2.350 (2) Å in $Cu(3\text{-OH-1,5-DTCO})_2(ClO_4)_2$.[1]

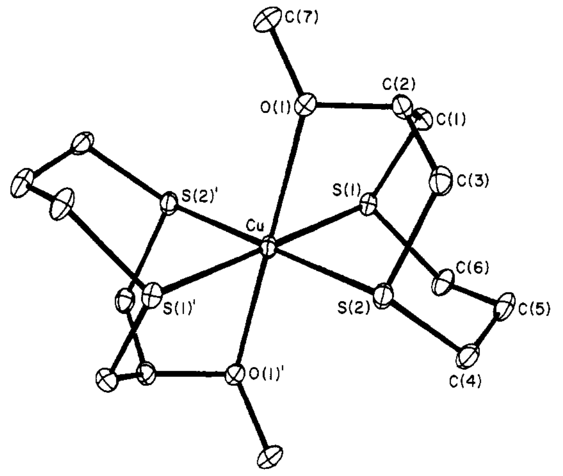

Figure 1. Perspective drawing of the bis(3-methoxy-1,5-dithiacyclooctane)copper(II) cation showing anisotropic thermal ellipsoids at the 50% level and the atom-numbering scheme.

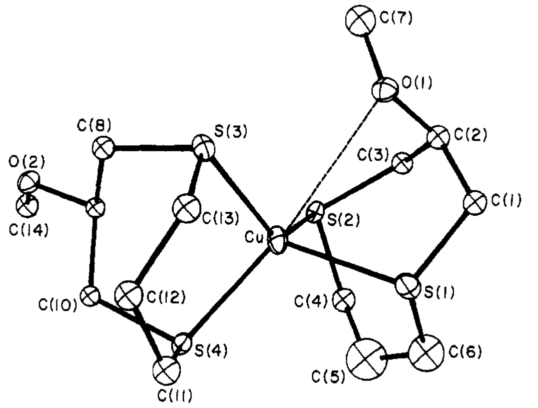

Figure 2. Perspective drawing of the bis(3-methoxy-1,5-dithiacyclooctane)copper(I) cation showing anisotropic thermal ellipsoids at the 50% level and the atom-numbering scheme.

$Cu(3\text{-OMe-1,5-DTCO})_2ClO_4{\cdot}CH_3OH$. As can be seen in Figure 2, the Cu(I) complex has a distorted-tetrahedral arrangement of four thioether sulfur atoms coordinated to the metal. An unusual feature of the structure is the presence of an intramolecular long-range electrostatic interaction between Cu and the methoxyl oxygen O(1). The distance of 3.069 (5) Å between these two atoms is too long for a weak covalent bond, but it is short enough to show a stereochemical effect. For example, if the interacting oxygen atom is included, the geometry around Cu can be described as roughly trigonal

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(4) Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1913–1918.

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(8) Olmstead, M. M., unpublished results.

bipyramidal, with an equatorial plane comprised of S(1), S(2), and S(3) and S–Cu–O angles of 72.9 (2), 72.4 (2), and 75.9 (2)°, respectively. Further, the opposing Cu–S(4) bond is 2.351 (2) Å, longer than any of the other Cu–S bonds (2.311 Å average). An examination of the interatomic distances and angles around O(1) is also revealing. In addition to its interaction with Cu, O(1) is involved in a hydrogen bond to the hydroxyl hydrogen of the lattice methanol molecule. The position of this hydrogen atom was determined from a difference map and was allowed to refine freely. It is therefore possible to examine all of the angles around O(1), and these are listed in Table III. Although some of the esd's are necessarily large, a reasonable disposition in space is obtained. On the basis of these results it appears that the methoxyl oxygen is located in a potential energy well that imparts an apparent trigonal-bipyramidal geometry to the Cu(I). By contrast, the methoxyl oxygen in the other chelate ring exhibits no tendency to interact with Cu(I).

Acknowledgment. We thank the National Science Foundation (Grant CHE-8015489) for support of this research.

Registry No. 3-OMe-1,5-DTCO, 86944-02-7; 3-OH-1,5-DTCO, 86944-00-5; Cu(3-OMe-1,5-DTCO)$_2$(ClO$_4$)$_2$, 91670-00-7; Cu(3-OMe-1,5-DTCO)$_2$ClO$_4$·CH$_3$OH, 91670-03-0.

Supplementary Material Available: Listings of interatomic distances, angles, hydrogen coordinates, anisotropic thermal parameters, and observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Ligand-Bridged Dimers. 2. Homobinuclear Derivatives of (Methylcyclopentadienyl)manganese Dicarbonyl[1]

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The solvent adducts (η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$·S (where S = diethyl ether, tetrahydrofuran), which can be prepared photochemically[3] as in eq 1, serve as useful intermediates for the

$$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_3 \xrightarrow[\text{S}]{h\nu} (\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\text{·S} + \text{CO} \quad (1)$$

thermal syntheses of monosubstituted derivatives[4] of the tricarbonyl (eq 2). We have made use of this reactivity to extend

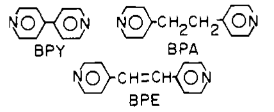
$$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\text{·S} \xrightarrow[\text{S}]{\text{X}} (\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\text{X} \quad (2)$$

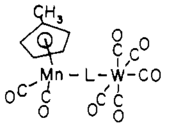
our work[1] on the syntheses of ligand-bridged dimers. In this paper we present the synthesis and characterization of the ligand-bridged dimers of the general formula [(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$]$_2$L, where L = 4,4′-bipyridine (BPY), 1,2-bis(4-pyridyl)ethylene (BPE), and 1,2-bis(4-pyridyl)ethane (BPA). We view the characterization of these compounds as a natural prelude to the synthesis and characterization of the heteronuclear ligand-bridged dimers shown in I, whose photochemistries we hope eventually to be able to study. Compounds of the type shown in I should be especially interesting because of known differences in the spectra and photoreactivities of the mononuclear compounds W(CO)$_5$X[5] and (η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$X.[6]

Table I. IR Spectroscopic Data[a]

compds	ν_{CO}, cm^{-1}
(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_3$	2018 (m), 1932 (s)
(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$·THF	1921 (s), 1848 (m)
[(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$]$_2$BPA	1921 (s), 1850 (s)
[(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$]$_2$BPY	1920 (s), 1852 (s)
[(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$]$_2$BPE	1928 (s), 1850 (s)

[a] In THF solution.





I

Experimental Section

Materials and Reagents. The starting tricarbonyl, (η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_3$, was obtained from Strem Chemicals and was distilled under vacuum and stored under argon prior to use. The ligands BPA and BPE were obtained from Aldrich and used without purification. The ligand BPY was obtained from Aldrich as the dihydrate and was purified by vacuum sublimation. All solvents were distilled from LiAlH$_4$, under argon. Solvents were transferred under argon with use of syringe techniques.

Photolyses were carried out with a 450-W Hanovia medium-pressure mercury vapor lamp that was housed in an Ace Glass quartz immersion well. The photolyses were performed at 0 °C and under a constant purge of argon. All of the products were handled under argon with use of standard Schlenk techniques, as well as in a minimum amount of dim red light.

Synthetic Procedures. The dimeric products were prepared by the general synthetic procedure in which the free ligand BPY, BPA, or BPE was reacted thermally in a dry THF solution of the solvent adduct (η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$·THF. The THF adduct had to be freshly prepared but was not isolated. A specific example where L = BPY is typical of all syntheses.

(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_3$, 0.6 mL (5.2 mmol), was photolyzed under argon, at 0 °C in previously distilled THF (270 mL) for 1 h or until an infrared spectrum showed complete conversion to the THF adduct (vide infra). A continuous stream of argon was bubbled through the solution during photolysis to purge carbon monoxide from the solution. During photolysis, the color changed from pale yellow to a deep burgundy characteristic of the solvent adduct, (η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$·THF. The THF solution was then transferred via syringe to a flask containing BPY 0.52 g (3.2 mmol), which had previously been purged with argon. Thermal reaction for typically 2 h resulted in a color change to red (yellow when L = BPA, purple when L = BPE). Solvent was removed by distillation, and the solid product was purified by multiple recrystallizations from THF/hexane.

Yields were 40–60% depending on the ligand used. Anal. (Galbraith) Calcd for [CH$_3$C$_5$H$_4$Mn(CO)$_2$]$_2$N$_2$C$_{10}$H$_8$: C, 58.22; H, 4.14, N, 5.22. Found: C, 57.80; H, 4.22, N, 6.04. Calcd for

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(1) For the preceding paper, see: Gaus, P. L.; Boncella, J. M.; Rosegren, K. S.; Funk, M. O. *Inorg. Chem.* **1982**, *21*, 2174–2178.

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