leads to Pd(II) polyiodides rather than Pd(IV) complexes. It is interesting to recall that [Pd(o-C_6H_4($AsMe_2$)$_2$)X_2] and [Pd($Me_2As(CH_2)_3AsMe_2$)X_2][1] (X = Cl, Br) give Pd(IV) complexes on halogen oxidation. Chlorination of [Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)Cl_2] also produces the Pd(IV) analogue (Experimental Section), but [Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)Br_2] does not react with Br_2, behavior identical with that reported for the Pd(II) complexes of $Ph_2PCH_2CH_2PPh_2$.[1] The [Pd(L–L)X_2] (X = Cl, Br) complexes of the dithioether ligand do not oxidize on treatment with halogen.[13]

Acknowledgment. The authors wish to thank Dr. M. B. Hursthouse for X-ray data collection on the SERC/QMC Enraf-Nonius CAD-4 diffractometer and the University of Southampton for financial support (D.J.G. and L.R.G.).

Registry No. Pd($Me_2As(CH_2)_3AsMe_2$)I_2, 86272-79-9; Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_2, 57255-07-9; Pd($Me_2NCH_2CH_2NMe_2$)I_2, 86272-80-2; Pd(o-$C_6H_4(SbPh_2)_2$)I_2, 61872-22-8; Pd(o-$C_6H_4(SPh)_2$)I_2, 71499-01-9; Pd($Me_2As(CH_2)_3AsMe_2$)I_4, 86272-81-3; Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_4, 86272-82-4; Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)Cl_4, 86272-83-5; Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)Cl_2, 57255-05-7; Pd(o-$C_6H_4(AsMe_2)_2$)$_2I_6$, 86272-84-6; Pd(o-$C_6H_4(AsMe_2)_2$)$_2I_2$, 59110-23-5.

Supplementary Material Available: Tables III–VI giving isotropic and anisotropic temperature factors, H atom coordinates, equations of planes, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Contribution from the Molecular Structure Center and Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Isolation and Molecular Structures of Dinuclear [Mo($NC_6H_4CH_3$)(μ-S)($S_2CN(i\text{-}C_4H_9)_2$)]$_2$ and Cubane-like [Mo($NC_6H_4CH_3$)(μ_3-S)($S_2CN(i\text{-}C_4H_9)_2$)]$_4$, Two Oligomers in Equilibrium

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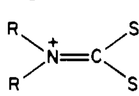
The reaction of [Mo($NC_6H_4CH_3$)(μ_3-S)($S_2P(OC_2H_5)_2$)]$_4$ and $S_2CN(i\text{-}C_4H_9)_2^-$ produces yellow [Mo($NC_6H_4CH_3$)(μ-S)($S_2CN(i\text{-}C_4H_9)_2$)]$_2$ and red [Mo($NC_6H_4CH_3$)(μ_3-S)($S_2CN(i\text{-}C_4H_9)_2$)]$_4$. The dinuclear compound crystallizes in the space group $P2_1/c$ with a = 17.73 (1) Å, b = 9.805 (5) Å, c = 22.89 (2) Å, β = 91.45 (3)°, and Z = 4. Final residuals were $R(F)$ = 0.063 and $R_w(F)$ = 0.055. The tetranuclear compound crystallizes in the space group $P2_1/n$ with a = 18.15 (1) Å, b = 17.64 (1) Å, c = 25.63 (1) Å, β = 105.12 (3)°, and Z = 4. Final residuals were $R(F)$ = 0.079 and $R_w(F)$ = 0.079. The structure of the former is similar in many respects to those of [MoX(μ-S)L]$_2$ (X = O, S; L = bidentate ligand) while the [Mo(μ_3-S)]$_4$ core of the latter mimics that found in the cubane-like [Mo($NC_6H_4CH_3$)(μ_3-S)($S_2P(OC_2H_5)_2$)]$_4$ complex. The equilibrium between the oligomers in solution is supported both by their isolation from the same reaction mixture and by spectroscopic evidence.

Introduction

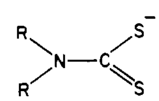
The isolation[1] and structural characterization[2] of the cubane-like tetranuclear compound [Mo($NC_6H_4CH_3$)(μ_3-S)($S_2P(OC_2H_5)_2$)]$_4$ were reported previously. These results are noteworthy and unusual because the authenticated[3] structure of [MoO(μ-S)($S_2P(O\text{-}i\text{-}C_3H_7)_2$)]$_2$ indicates that the existing analogies[4] in the structures of mononuclear arylimido and oxo compounds do not necessarily persist with polynuclear compounds. The tetranuclear nature of the arylimido compound was also defined by a molecular weight measurement for a rather concentrated solution.[1] In dilute solutions, however, the absorbances arising from a band at 585 nm deviate from the Beer–Lambert law in such a way that the equilibrium in eq 1 was postulated to account for the deviation.[1]

$$2[\mathrm{Mo}(\mathrm{NC_6H_4CH_3})(\mu\text{-S})(\mathrm{S_2P(OC_2H_5)_2})]_2 \rightleftarrows [\mathrm{Mo}(\mathrm{NC_6H_4CH_3})(\mu_3\text{-S})(\mathrm{S_2P(OC_2H_5)_2})]_4 \quad (1)$$

With the link between the degree of oligomerization and the identity of the multiply bound terminal ligand (O or NR) at least tentatively established (but with further examination clearly required), the influence of the bidentate ligand on the degree of oligomerization presented the next challenge that we wished to address. If the dithiophosphate ligands of the arylimido compound were replaced by dithiocarbamate ligands, the identity of the immediate coordination environment about each metal atom would be unchanged but other influences would be altered drastically. The valence angles around the phosphorus atoms of the dithiophosphate ligands force one of each pair of alkyl substituents to lie along the Mo–S bonds which are reponsible for binding two dinuclear molecules into a tetranuclear unit. The expected planar skeletons of the dithiocarbamate ligands would result in substantially lessened steric effects and provide a measure of increased stability for a tetranuclear compound. However, the resonance form given by **1**, whose importance would be evident from the planarity

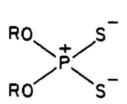


1

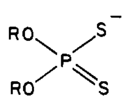


2

of the skeleton, should provide more electron density to each metal atom than **2** and its equivalent canonical form. The additional electron density would be expected to enhance the stability of the dinuclear compound since it can be utilized by the empty orbital on each molybdenum atom. In contrast, we do not believe that **3** contributes significantly to the stability



3



4

of the dinuclear dithiophosphate compound. The importance of multiple bonding at the phosphorus atom leads us to believe that **4** and its equivalent canonical form would make a much larger contribution.

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0020-1669/83/1322-2366$01.50/0

Table I. Crystal Data

	$[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$	$[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$
space group	$P2_1/c$	$P2_1/n$
temp, °C	−165	−171
a, Å	17.73 (1)	18.15 (1)
b, Å	9.805 (5)	17.64 (1)
c, Å	22.89 (2)	25.63 (1)
β, deg	91.45 (3)	105.12 (3)
Z	4	4
V, Å^3	3978.0	7919.6
d_{calcd}, g/cm^3	1.461	1.468
cryst size, mm	0.084 × 0.038 × 0.088	0.15 × 0.30 × 0.30
radiation	Mo Kα (0.710 69 Å)	Mo Kα (0.710 69 Å)
no. of unique data	5193	7397
no. of data with $F > 2.33\sigma(F)$	3712	5645
linear abs coeff	9.448	9.496
$R(F)$	0.063	0.079
$R_w(F)$	0.055	0.079
goodness of fit	1.129	1.773
largest Δ/σ	0.05	0.05

This paper described our efforts to bring the desired replacement to fruition, our eventual isolation of both $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$ and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$ from the same reaction mixture, the molecular structure of each, and the proof of the equilibrium between these oligomers.

Experimental Section

Reagents and Procedures. The preparation of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ by a one-pot method has been described previously[5] while $Na[S_2CN(i\text{-}C_4H_9)_2]\cdot xH_2O$ was prepared in a straightforward fashion from $(i\text{-}C_4H_9)_2NH$, CS_2, and NaOH.

Infrared spectra were obtained as KBr pellets with a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were recorded with the use of either a Varian HR-220 or a Varian XL-100 spectrometer. Electronic spectra were obtained from a Cary 14 spectrophotometer. Analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN.

$[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$ and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$. With use of standard vacuum line techniques, a THF solution of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and $Na[S_2CN(i\text{-}C_4H_9)_2]\cdot xH_2O$ in an approximate mole ratio of 1:4 was stirred for 15 min without a perceptible change in color. The solvent was then removed by distillation and the system was opened to the air. The addition of methyl alcohol and filtration allowed the green mixture of products to be isolated. Recrystallization was accomplished from a mixture of CH_2Cl_2 and methyl alcohol. Anal. Calcd: C, 43.9; H, 5.8; N, 6.4; S, 22.0. Found: C, 43.9; H, 5.7; N, 6.3; S, 22.2.

Yellow needles of the dinuclear compound were obtained by allowing slow diffusion of methyl alcohol that had been carefully layered on a solution of the mixture of products in acetone. Selected IR: 1495 (s), 1474 (m), 1439 (m), 1385 (w), 1366 (w), 1333 (m), 1251 (m), 1192 (w), 1149 (m), 1094 (w) cm^{-1}. Red plates of the tetranuclear compound were obtained by substituting CH_2Cl_2 for acetone and following the same procedure. A few yellow needles were sometimes obtained, but these could be removed manually. Selected IR: 1482 (s), 1462 (s), 1421 (m), 1385 (w), 1367 (w), 1353 (w), 1333 (m), 1318 (m), 1244 (m), 1193 (w), 1145 (m), and 1094 (w) cm^{-1}. ^1H NMR spectra of these compounds in CD_2Cl_2 were identical: δ 1.00 (t, bidentate ligand CH_3), 2.09 (s, aryl CH_3), 2.38 (n, CH), 3.80 (d, CH_2), 6.51 (s, aryl H).

Crystallography. General procedures and computational techniques have been described previously.[6]

A small crystal of the dinuclear compound was obtained by cleaving a larger crystal. The crystal was then transferred to the low-temperature device of the goniostat under an atmosphere of dry nitrogen. Crystal data are given in Table I. A total of 5891 reflections were collected with use of standard moving-crystal–moving-detector techniques using the following conditions: scan speed 4.0° min^{-1}; scan width 2.0° + dispersion; single background time at extremes of scan 4 s; aperture size 3.0 × 4.0 mm. The limits of the data collection were $6° < 2\theta < 45°$.

The structure was solved by means of a combination of direct and Fourier techniques. All non-hydrogen atoms were located and refined by full-matrix least-squares methods using anisotropic thermal parameters. All hydrogen atoms were located in a difference Fourier synthesis and refined with isotropic thermal parameters in the final cycles. An absorption correction was performed. The final difference Fourier map was essentially featureless with the largest peak being 0.83 e Å^{-1}.

A crystal of the tetranuclear compound, obtained by cleaving a larger crystal, was handled in an analogous fashion. Crystal data are again given in Table I. A total of 9048 reflections, including redundancies, were collected under the following conditions: scan speed 4.0° min^{-1}; scan width 1.7° + dispersion; single background time at extremes of scan 3 s; aperture size 3.0 × 4.0 mm. The limits of data collection were $6° < 2\theta < 40°$.

The structure was solved once again by direct methods and Fourier techniques. All non-hydrogen atoms were located and refined by full-matrix least-squares methods using anisotropic thermal parameters on all Mo and S atoms and isotropic thermal parameters for the remainder. No hydrogen atoms were located or included during the calculations. No absorption correction was performed. The largest peak (2.1 e Å^{-1}) in the final difference Fourier map was located close to a Mo atom, but the map was essentially featureless elsewhere.

Final values of the fractional coordinates are given in Table II for the dinuclear compound and in Table III for the tetranuclear compound. Observed and calculated structure amplitudes, thermal parameters, complete listings of all bond distances and angles for both compounds, and an ORTEP drawing of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN)(i\text{-}C_4H_9)_2)]_4$ are available as supplementary material.

Results and Discussion

Preliminary Experiments. The original synthesis of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ employed the key intermediate $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$.[1] Attempts to prepare an analogous dithiocarbamate compound by identical preparative procedures resulted in substances that we were unable to characterize. Substances that resisted characterization were also obtained after attempts to bring about the one-electron reduction of $[Mo(NC_6H_4CH_3)(S_2CN(C_2H_5)_2)_3]PF_6$.[7] Finally, however, we found that the direct reaction of the original tetranuclear compound with $Na[S_2CN(C_2H_5)_2]$ gave a yellow, sparingly soluble substance, $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(C_2H_5)_2)]_n$, with excellent analytical results.

In order to obtain a better solubility, reactions with dithiocarbamate ligands with alkyl substituents (R) of increasing complexity were examined. Light green, yellow, and green products were obtained with R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, and $i\text{-}C_4H_9$, respectively, with increasing solubilities and excellent analytical results. Microscopic examination of the product with R = $i\text{-}C_4H_9$ indicated that it was composed of a mixture of small yellow and red crystals. Because of the yellow colors of the dinuclear oxo compounds containing the MoS_2Mo core and the red color of the original tetranuclear compound, it appears that we have attained the unusual position of obtaining different oligomers of the same monomer. Finally, the correct choice of solvent and conditions for recrystallization allowed the isolation of either of these compounds without exceptional contamination from the other.

Structure of $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$. The X-ray structural determination of the yellow compound confirmed that it was indeed the dinuclear compound as shown in Figure 1. Some selected bond distances and angles are given in Tables IV and V.

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Table II. Final Positional Parameters ($\times 10^4$) for $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$

atom	x	y	z
Mo(1)	6706.7 (5)	1783 (1)	1609.1 (4)
Mo(2)	8017.7 (5)	3031 (1)	1202.6 (4)
S(3)	7936 (1)	1593 (3)	2000 (1)
S(4)	6769 (1)	3780 (3)	1068 (1)
S(5)	6349 (1)	997 (3)	2593 (1)
S(6)	5383 (1)	2471 (3)	1792 (1)
C(7)	5465 (5)	1738 (10)	2472 (4)
N(8)	4942 (4)	1748 (8)	2869 (3)
C(9)	4229 (5)	2509 (10)	2769 (4)
C(10)	3526 (5)	1595 (10)	2778 (4)
C(11)	2832 (5)	2484 (12)	2670 (5)
C(12)	3562 (6)	420 (12)	2341 (5)
C(13)	5041 (5)	1103 (10)	3447 (4)
C(14)	5120 (6)	2128 (12)	3946 (5)
C(15)	5202 (7)	1346 (13)	4513 (5)
C(16)	5804 (9)	3036 (15)	3862 (5)
S(17)	8334 (1)	5462 (3)	1065 (1)
S(18)	9347 (1)	3460 (3)	1541 (1)
C(19)	9256 (5)	5104 (10)	1299 (4)
N(20)	9817 (4)	6008 (8)	1313 (3)
C(21)	10581 (5)	5627 (10)	1499 (4)
C(22)	11176 (6)	6079 (11)	1066 (5)
C(23)	11943 (6)	5677 (12)	1326 (5)
C(24)	11014 (6)	5441 (12)	461 (5)
C(25)	9672 (6)	7464 (11)	1204 (5)
C(26)	9777 (5)	8315 (10)	1760 (4)
C(27)	9223 (6)	7870 (11)	2211 (5)
C(28)	9675 (6)	9817 (11)	1620 (5)
N(29)	6579 (4)	441 (8)	1132 (4)
C(30)	6568 (5)	−489 (10)	674 (4)
C(31)	6029 (5)	−349 (10)	223 (4)
C(32)	6012 (6)	−1243 (11)	−247 (4)
C(33)	6524 (5)	−2264 (10)	−287 (4)
C(34)	7048 (6)	−2402 (11)	171 (5)
C(35)	7086 (5)	−1522 (11)	634 (4)
C(36)	6502 (6)	−3213 (13)	−809 (5)
N(37)	8197 (4)	2115 (8)	582 (3)
C(38)	8259 (5)	1231 (10)	102 (4)
C(39)	7712 (5)	1251 (11)	−337 (5)
C(40)	7781 (6)	403 (12)	−812 (5)
C(41)	8381 (6)	−467 (12)	−863 (5)
C(42)	8917 (6)	−513 (12)	−408 (5)
C(43)	8858 (6)	328 (11)	63 (5)
C(44)	8450 (7)	−1417 (14)	−1376 (6)
H(1)	424 (4)	327 (9)	309 (4)
H(2)	427 (6)	292 (11)	233 (4)
H(3)	356 (5)	129 (10)	318 (4)
H(4)	274 (4)	313 (8)	301 (3)
H(5)	287 (5)	286 (10)	231 (4)
H(6)	239 (6)	176 (13)	270 (5)
H(7)	313 (6)	−2 (11)	240 (5)
H(8)	359 (5)	88 (11)	202 (4)
H(9)	405 (4)	1 (8)	244 (3)
H(10)	459 (5)	49 (10)	348 (4)
H(11)	550 (4)	59 (8)	343 (3)
H(12)	475 (8)	261 (14)	396 (6)
H(13)	482 (6)	69 (12)	457 (5)
H(14)	561 (7)	81 (13)	454 (5)
H(15)	521 (5)	204 (10)	481 (4)
H(16)	617 (10)	272 (18)	383 (8)
H(17)	572 (6)	373 (12)	352 (5)
H(18)	585 (6)	357 (13)	421 (5)
H(19)	1077 (5)	613 (10)	186 (4)
H(20)	1059 (5)	464 (9)	156 (4)
H(21)	1112 (6)	701 (12)	93 (5)
H(22)	1192 (4)	473 (8)	138 (3)
H(23)	1232 (6)	582 (12)	103 (5)
H(24)	1205 (5)	630 (10)	171 (4)
H(25)	1045 (5)	559 (9)	30 (4)
H(26)	1138 (4)	575 (8)	25 (3)
H(27)	1110 (4)	451 (8)	51 (3)
H(28)	998 (4)	789 (8)	91 (3)
H(29)	921 (4)	759 (8)	108 (3)
H(30)	1037 (6)	813 (12)	192 (5)
H(31)	933 (5)	811 (10)	258 (4)
H(32)	868 (5)	804 (10)	213 (4)
H(33)	924 (5)	709 (9)	227 (4)
H(34)	987 (4)	1041 (8)	197 (3)
H(35)	999 (6)	1030 (12)	140 (5)
H(36)	920 (5)	987 (10)	143 (4)
H(37)	570 (4)	24 (8)	25 (3)
H(38)	572 (4)	−113 (8)	−55 (3)
H(39)	734 (4)	−306 (8)	15 (3)
H(40)	738 (4)	−163 (9)	95 (4)
H(41)	610 (7)	−333 (13)	−90 (5)
H(42)	676 (6)	−296 (12)	−109 (5)
H(43)	665 (5)	−403 (9)	−68 (4)
H(44)	733 (5)	193 (10)	−35 (4)
H(45)	735 (5)	34 (9)	−114 (4)
H(46)	923 (4)	−124 (8)	−40 (3)
H(47)	921 (5)	36 (10)	34 (4)
H(48)	810 (7)	−198 (13)	−140 (5)
H(49)	841 (5)	−107 (10)	−170 (4)
H(50)	903 (6)	−189 (12)	−136 (5)

A distorted square pyramidal geometry around each molybdenum atom prevails if the metal–metal bond is excluded. Each metal atom is displaced from the best least-squares plane defined by the bridging sulfur atoms and the sulfur atoms of the bidentate ligand by 0.670 (3) Å toward the arylimido ligands. The MoS_2Mo core is not planar since each sulfur atom lies 0.201 (3) Å out of the best least-squares plane while the metal atoms are displaced by the same distance on the other side of that plane. The dihedral angle between the planes defined by the bridging sulfur atoms and each metal atom is 148°. Values ranging between 147 and 153° have been found previously for this angle for $[MoX(\mu\text{-}S)L]_2$ ($X = O$, $L = S_2P(O\text{-}i\text{-}C_3H_7)_2$,[3] $S_2CN(n\text{-}C_4H_9)_2$,[8] $S_2C_2(CN)_2$;[9] $X = S$, $L = S_2CN(n\text{-}C_4H_9)_2$[10]), where square-pyramidal geometry also prevails for each metal atom.

The bridging sulfur atoms are not arranged symmetrically between the molybdenum atoms with Mo(1)–S(3) and Mo(2)–S(4) having values of 2.343 (3) and 2.345 (3) Å, respectively, while Mo(1)–S(4) and Mo(2)–S(3) are 2.321 (3) and 2.313 (3) Å. Only the last examples fall within the 2.30–2.32-Å range found for $[MoX(\mu\text{-}S)L]_2$.[3,8-10] The aver-

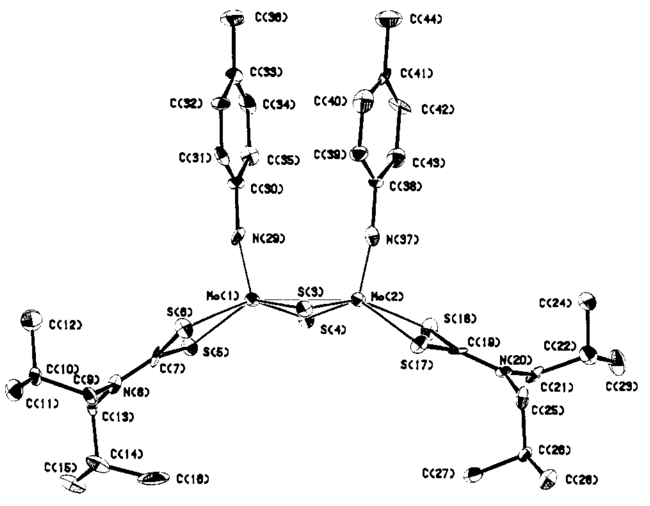

Figure 1. ORTEP drawing of $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$. Thermal ellipsoids are drawn at 50% probability.

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Table III. Final Positional Parameters for $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$

atom	*x*	*y*	*z*
Mo(1)	8283 (1)	2087 (1)	5762 (1)
Mo(2)	8120 (1)	3337 (1)	6446 (1)
Mo(3)	6342 (1)	2838 (1)	5492.5 (5)
Mo(4)	7304 (1)	3707 (1)	4981 (1)
S(5)	7395 (2)	2196 (2)	6294 (1)
S(6)	8657 (2)	3370 (2)	5684 (1)
S(7)	6934 (2)	4033 (2)	5783 (1)
S(8)	7072 (2)	2390 (2)	4915 (1)
S(9)	8795 (2)	1756 (2)	4962 (2)
S(10)	7821 (2)	798 (2)	5415 (2)
S(11)	7365 (2)	3755 (2)	7081 (2)
S(12)	8420 (2)	4714 (2)	6709 (1)
S(13)	5835 (2)	1517 (2)	5553 (2)
S(14)	5649 (2)	2773 (2)	6230 (2)
S(15)	8121 (2)	3505 (2)	4347 (1)
S(16)	8134 (2)	4878 (2)	4963 (1)
C(17)	8343 (8)	907 (8)	4937 (6)
N(18)	8350 (7)	379 (7)	4563 (5)
C(19)	8778 (9)	502 (9)	4153 (6)
C(20)	8297 (10)	972 (10)	3665 (7)
C(21)	7538 (10)	582 (10)	3382 (7)
C(22)	8819 (11)	1083 (11)	3275 (8)
C(23)	7974 (8)	−368 (8)	4576 (6)
C(24)	8563 (13)	−989 (12)	4840 (9)
C(25)	9150 (14)	−817 (14)	5337 (10)
C(26)	8044 (13)	−1719 (13)	4891 (9)
C(27)	7864 (8)	4622 (9)	7151 (6)
N(28)	7796 (6)	5126 (6)	7520 (5)
C(29)	8239 (9)	5830 (9)	7582 (6)
C(30)	7857 (10)	6435 (10)	7146 (7)
C(31)	7026 (10)	6600 (10)	7142 (7)
C(32)	8372 (10)	7158 (10)	7241 (7)
C(33)	7309 (9)	4969 (9)	7887 (6)
C(34)	7843 (12)	4687 (12)	8472 (9)
C(35)	8452 (12)	4155 (12)	8429 (8)
C(36)	7169 (11)	4292 (11)	8697 (8)
C(37)	5418 (8)	1825 (8)	6036 (6)
N(38)	4978 (6)	1410 (6)	6266 (5)
C(39)	4650 (9)	1712 (9)	6683 (6)
C(40)	3800 (9)	1944 (9)	6462 (7)
C(41)	3662 (10)	2598 (10)	6045 (7)
C(42)	3512 (11)	2193 (11)	6983 (8)
C(43)	4955 (9)	572 (9)	6182 (6)
C(44)	4196 (9)	283 (9)	5805 (6)
C(45)	4037 (9)	600 (9)	5232 (6)
C(46)	4232 (9)	−597 (9)	5789 (7)
C(47)	8454 (8)	4417 (8)	4465 (6)
N(48)	8929 (6)	4720 (6)	4209 (5)
C(49)	9148 (9)	4316 (9)	3768 (6)
C(50)	9979 (9)	4000 (10)	3957 (7)
C(51)	10042 (10)	3325 (10)	4358 (7)
C(52)	10167 (10)	3700 (11)	3419 (8)
C(53)	9213 (9)	5509 (9)	4325 (6)
C(54)	8587 (13)	6087 (13)	4027 (9)
C(55)	8173 (12)	5962 (12)	3449 (9)
C(56)	9011 (11)	6891 (11)	4141 (8)
N(57)	9078 (6)	1736 (6)	6222 (5)
C(58)	9760 (8)	1470 (8)	6540 (6)
C(59)	10409 (9)	1462 (9)	6353 (6)
C(60)	11135 (9)	1271 (9)	6695 (6)
C(61)	11200 (8)	1076 (8)	7234 (6)
C(62)	10537 (8)	1046 (8)	7437 (6)
C(63)	9815 (8)	1235 (9)	7092 (6)
C(64)	11974 (10)	906 (10)	7625 (7)
N(65)	8906 (6)	3083 (6)	6949 (4)
C(66)	9576 (8)	3012 (8)	7340 (6)
C(67)	9594 (9)	2804 (9)	7887 (6)
C(68)	10311 (9)	2681 (9)	8265 (7)
C(69)	10991 (8)	2751 (9)	8104 (6)
C(70)	11769 (10)	2569 (10)	8503 (7)
C(71)	10974 (8)	2986 (8)	7569 (6)
C(72)	10275 (9)	3119 (9)	7198 (6)
N(73)	5480 (6)	3107 (6)	5060 (4)
C(74)	4718 (8)	3181 (8)	4881 (6)
C(75)	4262 (8)	2620 (8)	4537 (6)
C(76)	3450 (8)	2711 (8)	4364 (6)
C(77)	3092 (8)	3351 (8)	4519 (6)
C(78)	3550 (8)	3911 (8)	4853 (6)
C(79)	4348 (8)	3848 (9)	5017 (6)
C(80)	2250 (9)	3433 (9)	4338 (6)
N(81)	6574 (6)	4091 (6)	4494 (4)
C(82)	6125 (8)	4551 (8)	4081 (6)
C(83)	5318 (8)	4538 (8)	3967 (6)
C(84)	4882 (9)	5000 (9)	3553 (6)
C(85)	5240 (9)	5466 (9)	3245 (6)
C(86)	6030 (9)	5447 (9)	3350 (6)
C(87)	6485 (8)	5016 (8)	3769 (6)
C(88)	4769 (9)	5917 (9)	2759 (7)

Table IV. Some Selected Bond Distances (Å) for $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$

Mo(1)-Mo(2)	2.807 (2)		
Mo(1)-S(3)	2.343 (3)	Mo(1)-S(6)	2.488 (3)
Mo(1)-S(4)	2.321 (3)	Mo(2)-S(17)	2.471 (3)
Mo(2)-S(3)	2.313 (3)	Mo(2)-S(18)	2.499 (3)
Mo(2)-S(4)	2.345 (3)	Mo(1)-N(39)	1.722 (8)
Mo(1)-S(5)	2.478 (3)	Mo(2)-N(37)	1.717 (8)

Table V. Some Selected Bond Angles (deg) for $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$

S(3)-Mo(1)-S(4)	102.3 (1)	S(3)-Mo(2)-N(37)	110.5 (3)
S(3)-Mo(2)-S(4)	102.5 (1)	S(4)-Mo(2)-N(37)	104.4 (3)
Mo(1)-S(3)-Mo(2)	74.2 (1)	S(5)-Mo(1)-N(37)	107.8 (3)
Mo(1)-S(4)-Mo(2)	73.9 (1)	S(6)-Mo(1)-N(37)	101.8 (3)
S(5)-Mo(1)-S(6)	70.6 (1)	S(17)-Mo(2)-N(37)	110.6 (3)
S(17)-Mo(2)-S(18)	70.2 (1)	S(18)-Mo(2)-N(37)	98.7 (3)
S(3)-Mo(1)-N(29)	106.7 (3)	Mo(1)-N(29)-C(30)	168.5 (7)
S(4)-Mo(1)-N(29)	108.3 (3)	Mo(2)-N(37)-C(38)	171.4 (7)

age[11] Mo–S–Mo and S–Mo–S angles are 74.1 (2) and 102.3 (0)°, which may be compared to 74.6–75.9 and 100.6–102.0° ranges found for the other compounds.

There is also an absence of symmetry in the distances in the bonds between the metal atoms and the sulfur atoms of the dithiocarbamate ligands. The shorter bonds, 2.478 (3) Å for Mo(1)–S(5) and 2.471 (3) Å for Mo(2)–S(17), are opposite the shorter bonds between the metal atoms and the bridging sulfur atoms while the longer bonds, 2.488 (3) Å for Mo(1)–S(6) and 2.499 (3) Å for Mo(2)–S(18), are opposite the longer bonds in the bridge. For comparison, the average distances in $[MoO(\mu\text{-}S)(S_2CN(n\text{-}C_4H_9)_2)]_2$ and $[MoS(\mu\text{-}S)(S_2CN(n\text{-}C_4H_9)_2)]_2$ are 2.44 (1)[8] and 2.447 (4) Å,[10] respectively. The S(5)–Mo(1)–S(6) and S(17)–Mo(2)–S(18) angles are 70.6 (1) and 70.2 (1)°, which compare favorably, however, with the average angles of 70.7 (2) and 70.8(1)° found in the oxo[8] and sulfido[10] compounds.

The molybdenum–nitrogen bond lengths, 1.722 (8) and 1.717 (8) Å, are identical within experimental error and within the range of 1.70–1.75 Å reported previously for arylimido compounds containing $Mo\equiv N$ bonds.[2,4,5,12] Similarly, the Mo–N–C(aryl) angles of 168.5 (7) and 171.4 (7)° are within the range of 164–177° found in those compounds. Each of the aromatic ligands of the arylimido ligands is virtually planar while the dihedral angle between the rings is only 8°.

Each of the S_2CNC_2 fragments within the dithiocarbamate ligands is planar within experimental error but is skewed with respect to the best least-squares plane for all of the sulfur atoms by an average value of 39°. No other remarkable distances

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(11) Standard deviations for average bond lengths have been calculated from the differences between individual bond lengths and the average bond length. Estimated standard deviations for sums and differences have been obtained from standard procedures for the propagation of errors.

(12) Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1982**, *21*, 2101.

Table VI. Some Selected Bond Distances (Å) for $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$

Mo(1)-Mo(2)	2.879 (3)	Mo(4)-S(6)	2.707 (4)
Mo(3)-Mo(4)	2.883 (3)	Mo(1)-S(9)	2.532 (4)
Mo(1)-S(5)	2.376 (4)	Mo(1)-S(10)	2.505 (4)
Mo(1)-S(6)	2.385 (4)	Mo(2)-S(11)	2.497 (4)
Mo(2)-S(5)	2.380 (4)	Mo(2)-S(12)	2.540 (4)
Mo(2)-S(6)	2.401 (4)	Mo(3)-S(13)	2.525 (4)
Mo(3)-S(7)	2.394 (4)	Mo(3)-S(14)	2.532 (4)
Mo(3)-S(8)	2.365 (4)	Mo(4)-S(15)	2.494 (4)
Mo(4)-S(7)	2.395 (4)	Mc(4)-S(16)	2.563 (4)
Mo(4)-S(8)	2.359 (4)	Mo(1)-N(57)	1.72 (2)
Mo(1)-S(8)	2.710 (4)	Mo(2)-N(65)	1.71 (2)
Mo(2)-S(7)	2.667 (4)	Mo(3)-N(73)	1.73 (2)
Mo(3)-S(5)	2.665 (4)	Mo(4)-N(81)	1.71 (2)

Table VII. Some Selected Bond Angles (deg) for $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$

S(5)-Mo(1)-S(6)	102.9 (1)	S(5)-Mo(1)-N(57)	102.1 (5)
S(5)-Mo(2)-S(6)	102.1 (1)	S(6)-Mo(1)-N(57)	101.1 (5)
S(7)-Mo(3)-S(8)	102.1 (1)	S(5)-Mo(2)-N(65)	102.6 (5)
S(7)-Mo(4)-S(8)	102.3 (1)	S(6)-Mo(2)-N(65)	100.5 (5)
S(5)-Mo(1)-S(8)	85.0 (1)	S(7)-Mo(3)-N(73)	102.5 (5)
S(6)-Mo(1)-S(8)	86.3 (1)	S(8)-Mo(3)-N(73)	104.6 (5)
S(5)-Mo(2)-S(7)	88.0 (1)	S(7)-Mo(4)-N(81)	101.2 (5)
S(6)-Mo(2)-S(7)	84.4 (1)	S(8)-Mo(4)-N(81)	104.4 (5)
S(7)-Mo(3)-S(5)	87.7 (1)	S(9)-Mo(1)-N(57)	93.0 (5)
S(8)-Mo(3)-S(5)	86.2 (1)	S(10)-Mo(1)-N(57)	93.4 (5)
S(7)-Mo(4)-S(6)	83.6 (1)	S(11)-Mo(2)-N(65)	94.5 (5)
S(8)-Mo(4)-S(6)	86.9 (1)	S(12)-Mo(2)-N(65)	88.4 (5)
Mo(1)-S(5)-Mo(2)	74.5 (1)	S(13)-Mo(3)-N(73)	90.5 (5)
Mo(1)-S(6)-Mo(2)	74.0 (1)	S(14)-Mo(3)-N(73)	87.0 (5)
Mo(3)-S(7)-Mo(4)	74.0 (1)	S(15)-Mo(4)-N(81)	93.5 (5)
Mo(3)-S(8)-Mo(4)	75.2 (1)	S(16)-Mo(4)-N(81)	90.9 (5)
S(9)-Mo(1)-S(10)	70.2 (1)	Mo(1)-N(57)-C(58)	173 (1)
S(11)-Mo(2)-S(12)	70.2 (1)	Mo(2)-N(65)-C(66)	170 (1)
S(13)-Mo(3)-S(14)	69.6 (1)	Mo(3)-N(73)-C(74)	157 (1)
S(15)-Mo(4)-S(16)	69.6 (1)	Mo(4)-N(81)-C(82)	164 (1)

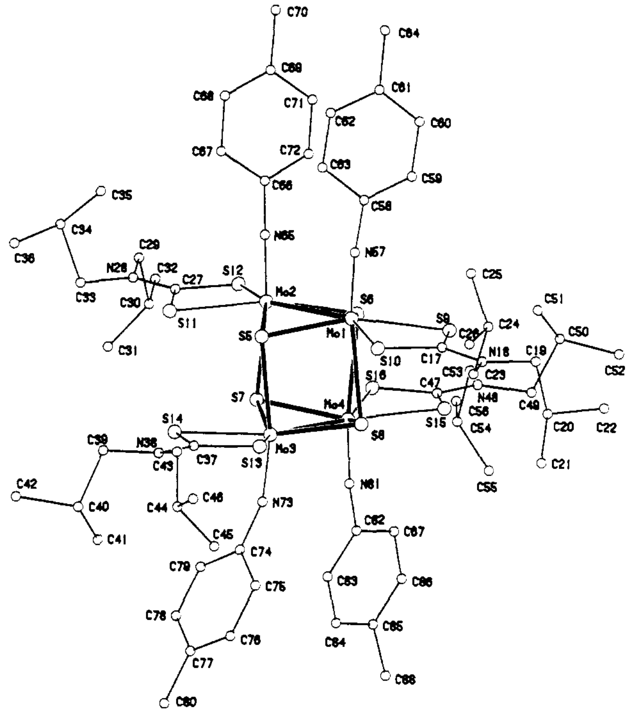

Figure 2. Ball-and-stick drawing of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$.

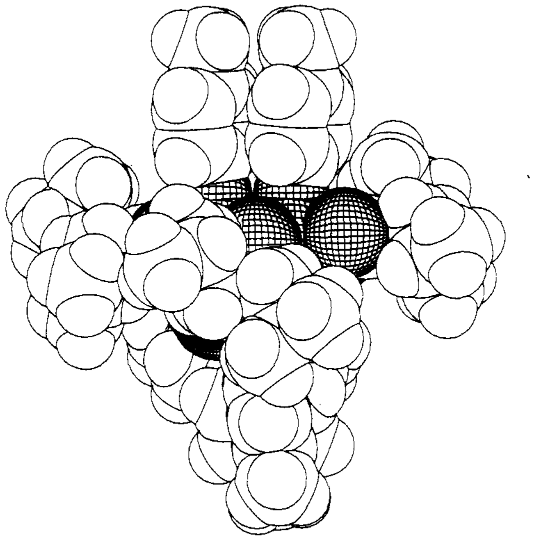

Figure 3. Space-filling molecular model of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$ which shows the juxtaposition of the adjacent arylimido ligands. The distorted pair of ligands occurs at the bottom of the drawing while the normal orientation appears at the top.

or angles occur within these ligands.

Structure of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$. The cubane-like structure of this compound is shown in Figure 2 and again by the space-filling model in Figure 3. Selected bond distances and angles can be found in Tables VI and VII.

If the metal–metal bonds are excluded, the coordination polyhedron around each molybdenum atom can be described as a distorted octahedron. The metal–metal distances can be separated into two sets. The first is a bonding set with an average bond distance of 2.881 (3) Å and the second a nonbonding set with an average distance of 3.66(4) Å. The molybdenum–sulfur bond lengths can be roughly partitioned into three sets. The first of these, which is specified by the bonds to the bridging sulfur atoms adjacent to the metal–metal bonds, has an average value of 2.38 (2) Å. The second set, which contains the four bonds to the sulfur atoms trans to the arylimido ligands, has an average value of 2.69 (3) Å. Bonds to the sulfur atoms of the dithiocarbamate ligands comprise the third set with an average value of 2.52 (2) Å.

The angles within the cube are also influenced by the presence of the metal–metal bonds. On the faces with these bonds, the average Mo–S–Mo angle is 74.4 (5)° while on the four remaining faces the average angle is 92 (1)°. Similarly, the S–Mo–S angles have an average of 102.4 (6) Å on the faces with metal–metal bonds but an average of 86 (2)° on the other faces.

The dihedral angle between the plane fitting Mo(1), S(5), and S(6) and the plane for Mo(2), S(5), and S(6) is 149° while the corresponding angle on the opposite face is 150°. The angle between the plane fitting Mo(1), Mo(2), S(7), and S(8) and that for Mo(3), Mo(4), S(5), and S(6) is 90°.

The molybdenum–nitrogen bond lengths are identical within experimental error with a value of 1.72 (1) Å. The aryl rings on one face of the cube are essentially parallel with a dihedral angle of only 5°. The Mo–N–C(aryl) angles on that face are normal with values of 173 (1) and 170 (1)°. However, a severe distortion occurs on the opposite face as shown clearly in Figure 3. Although one of the rings on that face is nearly in the expected location, the other is strongly twisted to give a dihedral angle of 79°. The distortion causes both Mo–N–C(aryl) angles to be low, with the one at 164 (1)° falling just within the 164–177° range while the other is 157 (1)°. Inspection of the packing within the unit cell has indicated that the twist of the aryl ring and the extra bending of this Mo–N–C(aryl) angle is the result of a nearby molecule. The twist in this ring and nonbonded repulsions cause the second ring to also bend slightly away.

The four S_2CNC_2 fragments within the dithiocarbamate ligands are essentially planar. The remainder of the bond lengths and angles within these ligands are unexceptional.

Table VIII. Some Average[a] Molecular Parameters for $[Mo(NC_6H_4CH_3)(\mu\text{-}S)L]_n$

	L		
	$S_2CN(i\text{-}C_4H_9)_2$	$S_2CN(i\text{-}C_4H_9)_2$	$S_2P(OC_2H_5)_2$[b]
n	2	4	4
Mo–Mo, Å	2.807 (2)	2.881 (3)	2.862 (1)
Mo–S_b, Å	2.33 (2)	2.38 (2) 2.69 (3)	2.366 (5) 2.70 (1)
Mo–S_l, Å	2.48 (2)	2.52 (2)	2.55 (1)
Mo–N, Å	1.720 (1)	1.72 (1)	1.72 (1)
Mo–S_b–Mo, deg	74.1 (2)	74.4 (5) 92 (1)	74.5 (2) 93 (1)
S_b–Mo–S_b, deg	102.3 (0)	102.4 (7) 86 (2)	102.0 (1) 85 (1)
S_l–Mo–S_l, deg	70.4 (3)	69.9 (3)	78.0 (6)
dihedral angles, deg[c]	148	150 (1) 90	148 (0) 90

[a] Reference 11. [b] Reference 2. [c] The larger angle pertains to the $Mo(S_b)_2$ planes while the smaller angle measures the angular deviation between a plane defined by two bonded metal atoms and the sulfur atoms on the opposite face and a plane defined by the remainder of the atoms in the core.

Comparisons. Several key average dimensions in the dinuclear and tetranuclear dithiocarbamate compounds are compared in Table VIII. The formation of four additional Mo–S bonds in the oligomerization and the resulting increase in the electron density around each metal atom leads to a significant increase in the length of the Mo–Mo bonds. Table VIII also includes a comparison of the average dimensions in the tetranuclear dithiocarbamate and dithiophosphate compounds and indicates that the metal–metal bond lengths in the latter have suffered a small but statistically significant decrease.

In addition to the lengths of the metal–metal bonds, three other comparisons would also be of interest. First, changes in the Mo–S_b (b = bridging) distances or the angles involving those atoms must accompany the increase in the length of the Mo–Mo bonds upon oligomerization in the dithiocarbamate system. The average dimensions of each molecule suggest that the Mo–S_b bonds that are common to both compounds have increased while the bond angles are essentially unchanged. Second, changes in the Mo–S_l (l = ligand) bond lengths should give some indication of the relative importance of **1** and **2** in each of the oligomers of the dithiocarbamate system. The average dimensions suggest that **1** assumes more importance in the dinuclear compounds, as predicted, because of a smaller average bond length. Third, changes in the lengths of the Mo–S_b bonds that are responsible for binding the dinuclear components into tetranuclear units should give some indication of the relative stabilities of the two tetranuclear compounds. The essentially identical bond distances suggest comparable stabilities if the energy released in the formation of these bonds is a dominant factor in the free energy of oligomerization. A statistical verification of these three conclusions based on average dimensions cannot be obtained, however, because the Mo–S_b and Mo–S_l bond lengths within each compound are so badly scattered that they fail to comply with χ^2 tests for statistical equality.[13] The failure of these tests, however, does not invalidate the conclusion that there is an overall dimensional similarity in the two tetranuclear compounds.

Spectroscopy and Its Significance. The infrared spectra of the dithiocarbamate compounds as obtained in KBr pellets differ considerably in the region between 1500 and 1000 cm^{-1} with the spectrum of the tetranuclear compound being more complicated. As a consequence of additional coupling, shifts in certain bands can be seen. For example, the absorption at 1482 cm^{-1} in the spectrum of the tetranuclear compound, a band which is one of several attributable to $\nu(CN)$ of the bidentate ligand, occurs at 1495 cm^{-1} in the spectrum of the dinuclear compound.

The ^1H NMR spectra of solutions of these compounds are identical, however. Moreover, the electronic spectrum of each of these compounds in solution contains a band at 586 nm with equal masses providing equal absorbances. These absorbances deviate significantly from the Beer–Lambert law.

When the spectroscopic evidence is coupled with the isolation of both oligomers from the same reaction mixture, the existence of a rapidly established equilibrium between the oligomers can hardly be doubted. This evidence provides excellent support for the specific equilibrium in eq 1. The ease with which both of the dithiocarbamate compounds were isolated also suggests that the equilibrium constant is much less than that for the dithiophosphate system, a conclusion which is not foreshadowed by any of the average dimensions in Table VIII. The evaluation of the equilibrium constant for this system as well as those for several other systems with various substituted arylimido ligands and various dithiocarbamate and dithiophosphate ligands will be treated in a subsequent paper.

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Registry No. $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2]_2$, 86128-95-2; $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2]_4$, 86128-96-3; $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2]_4$, 73037-71-5.

Supplementary Material Available: Listings of observed and calculated structure amplitudes, thermal parameters, and all bond distances and angles and an ORTEP drawing of the tetranuclear compound (94 pages). Ordering information is given on any current masthead page.

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