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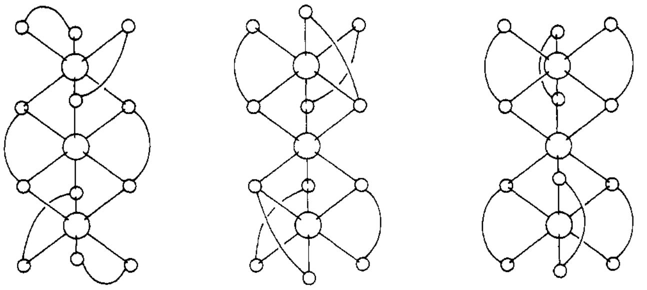


Figure 2. Schematic drawings of the coordination in $[Ni(acac)_2]_3$, $[Co(OCH_2CH_2NH_2)_2]_3^{2+}$, and $[Mn(acac)_2]_3$ chelates.

all the coordination polyhedra of the three nickel atoms were described as octahedra, shown in Figure 2.

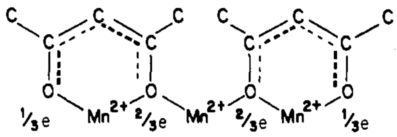
The average Mn–O distance in the central MnO_6 unit is 2.170 [4] Å, while the six Mn–O distances in the terminal MnO_6 unit are grouped into two classes with averages Mn(1)–O(*j*1) = 2.099 [2] Å and Mn(1)–O(*j*2) = 2.244 [9] Å; thus the Mn–O(bridging) distances are 0.145 Å longer than the Mn–O(nonbridging) distance. This large difference indicates that each of the ligands in this compound coordinates the Mn atom unsymmetrically.

The three independent ligand molecules are planar; deviations of the atoms from the least-squares mean planes are given in the supplementary material. The average angle between the mean planes is 120.0 [4]°. Corresponding bond distances and angles within the three ligands are very similar; however, the average distances noticed for C–O(nonbridging) and C–O(bridging) are 1.248 [5] and 1.278 [4] Å, respectively, and the average endocyclic C–C bond distance adjacent to the C–O(nonbridging) bond is 1.432 [7] Å and adjacent to the C–O(bridging) bond is 1.370 [3] Å. The differences are significant as compared with individual esd's. Associated with the discrepancies in distances mentioned above, two average angles of Mn–O–C, 130.5 [4] and 135.4 [4]°, are also found in Table II.

Discussion

As is well-known, many of the acetylacetone complexes of the first-row transition metals are polymeric, and now bis(acetylacetonato)manganese(II) has also been found to be trimeric, as is the nickel complex. It is very interesting that this chelate involves a trigonal-prismatic structure as D_{3h}–O_h–D_{3h} in contrast with O_h–O_h–O_h for the nickel complex as shown in Figure 2. A trigonal prism is predicted to be less stable than an octahedron because of the closer contacts between the six donor atoms. But this structure may be favored if chelates have large metal–ligand atom distances and small bite angles.

The first report of a trigonal-prismatic structure was on $Re(S_2C_2Ph_2)_3$[16] and $Mo(S_2C_2H_2)_3$[17] chelates. This structure was also revealed in tris(dipivaloylmethanate)erbium,[18] in which the oxygen atoms, instead of the sulfur atoms, coordinate the central atom. Polynuclear complexes containing trigonal-prismatic units were found in $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$, which is described as O_h–D_{3h}–O_h with the central cation of Co(II).[19] But in the central unit the metal is not chelated by the ligands. Thus trimeric $Mn(acac)_2$ is really the first example of a neutral chelate including trigonal-prismatic units, in which the metals are coordinated to the ligands, indicated as $[Mn(Mn(acac)_3)_2]$. The occurrence of the trigonal-prismatic structure may be due to less repulsive interaction between the neighboring oxygen atoms because of the rather small O–Mn–O bite angles with the large Mn–O distances. Of course, the octahedral structure of the central unit is understandable by considering the large repulsions between the methyl groups in the terminal ligands. Another special feature in the results of the trimeric $Mn(acac)_2$ is that the structure of the acetylacetone ligand is not symmetric. In monomeric chelates their structures should be symmetric[20] because the acac ligands resonate completely. However, in the trimeric $Mn(acac)_2$ chelate the formula



with unsymmetric formal charges on the ligand atoms, i.e., $^1/_3$ e and $^2/_3$ e on the nonbridging and bridging atoms, respectively, is expected if we assume the same oxidation states of three manganese ions and completely ionic bonding of Mn–O. Accordingly, the ligand resonates incompletely, as illustrated, yielding an unsymmetric structure with two different bond orders for C–O and C–C in agreement with their experimental bond distances. Such deformed structures of acac ligands are very common but have not been documented until now in spite of the reports on many of the polymeric acac chelates.[3-8]

Registry No. $Mn(acac)_2{\cdot}2H_2O$, 14024-80-7; $[Mn(acac)_2]_3$, 95978-22-6.

Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms, observed and calculated structure factors, and deviations of atoms from the least-squares planes (28 pages). Ordering information is given on any current masthead page.

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Isolation and Crystal Structure of the Cubane-like Cluster $[Cr_4(OH)_4(mhp)_8]$ (mhp = 6-Methyl-2-hydroxypyridinate)

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The mhp anion (Hmhp = 6-methyl-2-hydroxypyridine) has been shown in recent years to be versatile in its modes of binding to metal centers. In complexes $[M_2(mhp)_4]$, where M = Cr,[2,3] Mo,[2,4] W,[2] Ru,[5] Rh,[2,6,7] or Pd,[8] four mhp ligands bridge a pair of metal atoms in an arrangement with essentially D_{2d} symmetry, each metal atom bonding to two nitrogen and two oxygen atoms. The metal–metal separations in these complexes are among the shortest ever observed for each metal, although formal bond orders range from 4 (Cr, Mo, W) down to 0 (Pd). A different ar-

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each metal atom bonding to two nitrogen and two oxygen atoms. The metal–metal separations in these complexes are among the shortest ever observed for each metal, although formal bond orders range from 4 (Cr, Mo, W) down to 0 (Pd). A different arrangement of four mhp ligands about a dimetal center is found in many rhodium complexes of general formula $[Rh_2(mhp)_4L]$,[7,9] with a variety of axial ligands L attached to the rhodium atom, which is bonded to three mhp bridges through oxygen and to only one through nitrogen. Single mhp bridges spanning Cu(I)–Cu(I) separations of 2.656 (1)–2.709 (1) Å occur in $[Cu_4(mhp)_4]$.[10]

The mhp anion can also act as a bidentate ligand to a single metal atom.[11] Such groups can bridge to other metal centers: thus, in the dodecanuclear $[Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}]$ molecule, six of the chelating mhp ligands form an additional Co–O bond each and the other six form two such bonds.[12] In its protonated form, Hmhp can serve as a unidentate ligand, bonded through oxygen,[9] or as a bridging ligand in which oxygen is bonded simultaneously to two metal atoms.[13]

We now report the isolation and structural characterization of $[Cr_4(OH)_4(mhp)_8]$, a cubane-like cluster involving the longest span between two metal atoms so far observed for a bridging mhp ligand.

Table I. Refined Atomic Coordinates ($\times 10^4$)

atom	*x*	*y*	*z*
Cr	2257 (1)	3706 (1)	1972 (1)
O(1)	34 (3)	3281 (3)	2911 (2)
C(11)	−125 (4)	4121 (4)	2477 (2)
C(12)	−1207 (4)	4570 (5)	2459 (3)
C(13)	−1410 (5)	5504 (5)	2062 (3)
C(14)	−571 (5)	5997 (5)	1668 (3)
C(15)	466 (4)	5543 (4)	1670 (3)
C(16)	1387 (5)	6087 (5)	1246 (3)
N(1)	704 (3)	4583 (3)	2062 (2)
O(2)	2252 (2)	3842 (2)	846 (1)
C(21)	3089 (4)	3809 (4)	412 (2)
C(22)	3056 (4)	4186 (4)	−341 (3)
C(23)	3989 (5)	4136 (4)	−761 (3)
C(24)	4976 (4)	3740 (4)	−483 (2)
C(25)	5008 (4)	3349 (4)	230 (3)
C(26)	5983 (4)	2844 (6)	611 (3)
N(2)	4066 (3)	3408 (3)	657 (2)
H(2)	4017 (52)	2970 (53)	1312 (32)
O(3)	3529 (2)	2706 (2)	1961 (1)

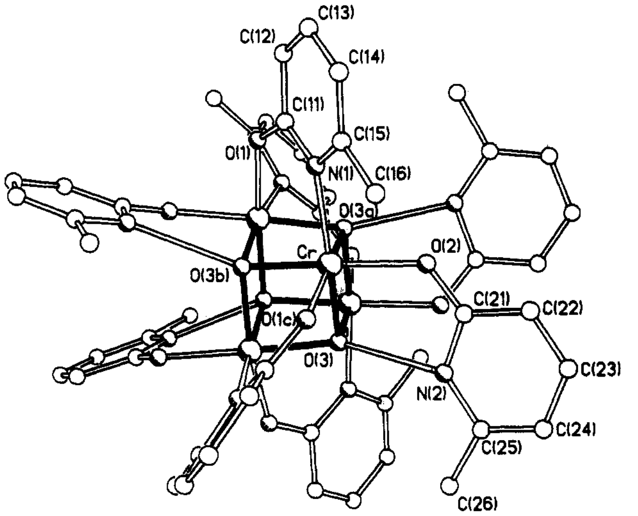

Figure 1. The $[Cr_4(OH)_4(mhp)_8]$ molecule, showing the atom-labeling scheme, including symmetry-related atoms bonded to Cr. Bonds within the Cr_4O_4 cluster are filled; others, open. The molecular S_4 axis runs horizontally.

Experimental Section

Preparation of $[Cr_4(OH)_4(mhp)_8]$. The complex was first obtained upon refluxing $[Cr(CO)_6]$ (2.0 g, 9 mmol) and Hmhp (4.0 g, 37 mmol) in diglyme (100 mL), previously dried over CaH_2, under an atmosphere of dinitrogen for 6 h. The initially yellow solution turned green and some small, dark green crystals were deposited on cooling to room temperature. Anal. Calcd for $C_{48}H_{52}Cr_4N_8O_{12}$: C, 50.5; H, 4.6; Cr, 18.2; N, 9.8. Found: C, 50.4; H, 4.8; Cr, 17.1; N, 9.3. This preparative procedure proved unreliable and an alternative route was sought. The title compound may be prepared by warming $[Cr_2(mhp)_4]\cdot nH_2O^2$ ($n \leq 1$) in dried diglyme or THF. Thus, a suspension of $[Cr_2(mhp)_4]\cdot H_2O$ (0.25 g, 0.045 mmol) in THF (25 mL), previously distilled from CaH_2, was maintained at ≤ 50 °C and stirred for ca. 48 h, whereupon a dark green solution apeared and a small quantity of precipitated $Cr(OH)_3$ was obtained. Evaporation of the THF, followed by dissolution in acetone, filtration, and evaporation to dryness produced a dark green powder of $[Cr_4(OH)_4(mhp)_8]$ contaminated with Hmhp; this impurity may be removed by extraction with hexane; yield ca. 0.15 g (ca. 60%).

Crystal Structure Determination. A crystal of size 0.21 × 0.23 × 0.31 mm was mounted in a glass capillary and investigated at room temperature on a Stoe-Siemens AED diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Unit cell dimensions were refined from 2θ values of 48 reflections ($20 < 2\theta < 25°$) centered at $\pm\omega$: $a = 12.082$ (1) Å and $c = 17.899$ (2) Å for the tetragonal cell, space group $P4_2/n$; $V = 2612.8$ Å^3 and $Z = 2$ for the tetrameric formula with $M_r = 1141.0$, $d_{calcd} = 1.450$ g cm^{-3}, and $\mu = 8.54$ cm^{-1}.

Data were collected in the ω/θ scan mode by a profile-fitting procedure,[14] for reflections with $2\theta < 50°$ and in the two octants with all indices ≥0 and with all indices <0. Of the 4785 reflections measured, 104 were systematically absent. No absorption corrections were applied. Averaging of equivalent reflections (merging $R = 0.027$) gave 2300 unique data, 1598 of which had $F > \sigma(F)$ and were used for structure determination and refinement.

The single independent Cr atom was located from a Patterson synthesis; other atoms were located from different syntheses.[15] Atomic scattering factors were taken from ref 16. Anisotropic thermal parameters were refined for all non-H atoms. H atoms of the mhp ligand were included in calculated positions (C–H = 0.96 Å, rigid methyl groups with H–C–H = 109.5°, aromatic H on external bisectors of ring angles) and assigned $U(H) = 1.2U_{eq}(C)$, where U_{eq} is the equivalent isotropic thermal parameter.[17] The H atom of the hydrogen bond between the μ_3-OH group and one of the mhp nitrogen atoms was located in a difference synthesis and refined freely. There were no indications of extinction. Final values of R and of $R' = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ were 0.059 and 0.057, respectively, with $w^{-1} = \sigma^2(F) + 0.0003F^2$. A normal probability plot[18] was linear, with slope 1.37. Maximum and mean values of shift/esd were 0.08 and 0.01 in the final cycles.

ESR and Magnetic Measurements. ESR spectra were obtained with a Varian E112 spectrometer system, in conjunction with an Oxford Instruments ESR9 cryostat. Spectral collection and integration were performed as described previously.[19] Room-temperature magnetic moments were obtained by the Gouy method.

Results and Discussion

Isolation of $[Cr_4(OH)_4(mhp)_8]$. The preparative procedure, which led initially to the formation of $[Cr_4(OH)_4(mhp)_8]$, corresponds to the route originally employed to synthesize $[W_2(mhp)_4]$ from $[W(CO)_6]$ and Hmhp in diglyme.[2] When [Cr(C-

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Table II. Bond Lengths (Å) and Angles (deg)[a]

Cr-N(1)	2.160 (4)	Cr-O(1c)	1.973 (3)
Cr-O(2)	2.020 (3)	Cr-O(3)	1.955 (3)
Cr-O(3a)	1.952 (3)	Cr-O(3b)	1.923 (3)
O(1)-C(11)	1.292 (6)	N(1)-C(11)	1.366 (6)
N(1)-C(15)	1.387 (6)	C(11)-C(12)	1.416 (7)
C(12)-C(13)	1.357 (8)	C(13)-C(14)	1.371 (8)
C(14)-C(15)	1.367 (8)	C(15)-C(16)	1.499 (8)
O(2)-C(21)	1.277 (5)	N(2)-C(21)	1.350 (6)
N(2)-C(25)	1.373 (6)	C(21)-C(22)	1.423 (6)
C(22)-C(23)	1.356 (7)	C(23)-C(24)	1.377 (8)
C(24)-C(25)	1.361 (6)	C(25)-C(26)	1.492 (8)
N(2)-H(2)	1.286 (59)	O(3)-H(2)	1.343 (58)

N(1)-Cr-O(2)	91.9 (1)	N(1)-Cr-O(3)	170.5 (1)
O(2)-Cr-O(3)	92.5 (1)	N(1)-Cr-O(1c)	99.1 (1)
O(2)-Cr-O(1c)	92.6 (1)	O(3)-Cr-O(1c)	89.2 (1)
N(1)-Cr-O(3a)	90.4 (1)	O(2)-Cr-O(3a)	93.5 (1)
O(3)-Cr-O(3a)	80.9 (1)	O(1c)-Cr-O(3a)	168.5 (1)
N(1)-Cr-O(3b)	90.0 (1)	O(2)-Cr-O(3b)	177.9 (1)
O(3)-Cr-O(3b)	85.5 (1)	O(1c)-Cr-O(3b)	88.0 (1)
O(3a)-Cr-O(3b)	85.6 (1)	C(11)-O(1)-Cr(b)	132.1 (3)
O(1)-C(11)-C(12)	116.8 (4)	O(1)-C(11)-N(1)	122.6 (4)
C(12)-C(11)-N(1)	120.6 (4)	C(11)-C(12)-C(13)	119.9 (5)
C(12)-C(13)-C(14)	119.8 (5)	C(13)-C(14)-C(15)	120.1 (5)
C(14)-C(15)-C(16)	120.2 (5)	C(14)-C(15)-N(1)	121.8 (5)
C(16)-C(15)-N(1)	117.9 (4)	Cr-N(1)-C(11)	118.5 (3)
Cr-N(1)-C(15)	123.6 (3)	C(11)-N(1)-C(15)	117.7 (4)
Cr-O(2)-C(21)	127.0 (3)	O(2)-C(21)-C(22)	123.0 (4)
O(2)-C(21)-N(2)	120.4 (4)	C(22)-C(21)-N(2)	116.6 (4)
C(21)-C(22)-C(23)	119.1 (5)	C(22)-C(23)-C(24)	122.4 (4)
C(23)-C(24)-C(25)	118.9 (5)	C(24)-C(25)-C(26)	126.4 (5)
C(24)-C(25)-N(2)	118.8 (4)	C(26)-C(25)-N(2)	114.9 (4)
C(21)-N(2)-C(25)	124.2 (4)	C(21)-N(2)-H(2)	113.8 (28)
C(25)-N(2)-H(2)	121.6 (28)	Cr-O(3)-Cr(a)	99.1 (1)
Cr-O(3)-Cr(c)	93.7 (1)	Cr(a)-O(3)-Cr(c)	93.8 (1)
Cr-O(3)-H(2)	101.9 (27)	Cr(a)-O(3)-H(2)	115.5 (27)
Cr(c)-O(3)-H(2)	143.7 (26)	N(2)-H(2)-O(3)	155.0 (55)

[a] Symmetry operator codes: (a) $^1/_2 - x$, $^1/_2 - y$, z; (b) $^1/_2 - y$, x, $^1/_2 - z$; (c) y, $^1/_2 - x$, $^1/_2 - z$.

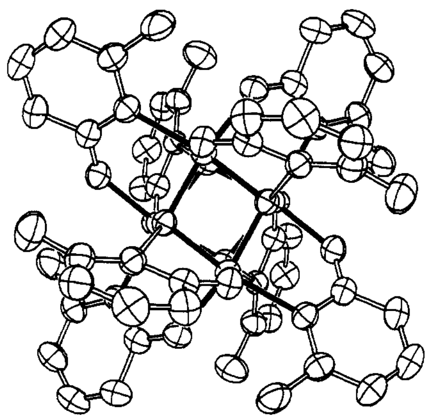

Figure 2. View down the S_4 axis (the crystallographic c axis), showing the thermal motion as 50% probability ellipsoids. Bonds to Cr are filled; others, open.

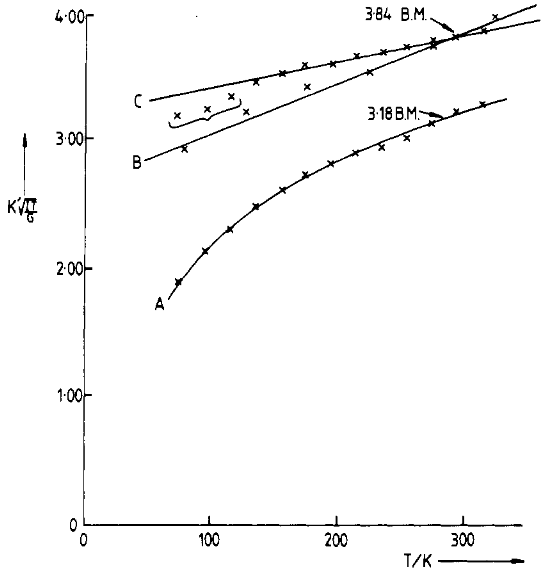

Figure 3. Variation of the relative intensity[19] of the ESR signal with temperature, for solid samples of $[Cr_4(OH)_4(mhp)_8]$ (A), $K_3[Cr(C_2O_4)_3]$ (B), and $Cr_2(SO_4)_3{\cdot}K_2SO_4{\cdot}24H_2O$ (C). I is the second integral of the ESR signal, T is the temperature in kelvins, G is the spectrometer gain setting, and K' is the parameter used to adjust the value of the magnetic moment at room temperature measured by ESR spectroscopy to that determined by the Gouy method.

$O)_6]$ and Hmhp are refluxed in dry diglyme, $[Cr_2(mhp)_4]$ is formed within ca. 0.5 h. If, however, the reflux is continued, the dimer decomposes and some $[Cr_4(OH)_4(mhp)_8]$ is formed. This route proved unpredictable, presumably because of the requirement for a critical amount of water during the reaction. Occasionally, the conversion of $[Cr_2(mhp)_4]$ to $[Cr_4(OH)_4(mhp)_8]$ was incomplete; on the other hand, when the reaction was accomplished in undried diglyme, the major product was $Cr(OH)_3$. The alternative preparation of the tetramer from $[Cr_2(mhp)_4]{\cdot}H_2O$[2] is more rational, at least in terms of the origin of half of the hydroxo groups of the product. However, we found that the extent of hydration of this material could be varied, from the monohydrate to essentially the anhydrous compound, without significantly affecting the course of the reaction. Therefore, we presume that the (relatively small) amounts of water required for the formation of $[Cr_4(OH)_4(mhp)_8]$, by both routes described in the Experimental Section, derive wholly or partially from adventitious water present on the surface of the glassware and in the solvents and gases in contact with the reactants.

Structure of $[Cr_4(OH)_4(mhp)_8]$. Atomic coordinates are given in Table I; bond lengths and angles, in Table II. The molecular structure is shown in Figures 1 and 2. The crystallographic asymmetric unit consists of one Cr atom, one OH group, and two mhp ligands. The complete molecule contains four units and has S_4 ($\bar{4}$) symmetry, the centroid of the molecule lying at $^1/_4$, $^1/_4$, $^1/_4$ (Figure 2).

The Cr_4O_4 central cluster is a distorted cube with eight Cr–O distances of 1.954 (3) Å (mean of two independent values) and four distances of 1.923 (3) Å. In addition to this slight tetragonal compression along the crystallographic c axis (approximately horizontal in Figure 1 and perpendicular to the paper in Figure 2), the Cr_4 tetrahedron is larger than the O_4 tetrahedron. There are two different Cr···Cr diagonals: 2.974 (1) Å across the two larger Cr_2O_2 faces and 2.829 (1) Å for the remaining four diagonals; the O_4 tetrahedron has four edges of 2.63 (1) Å and two of 2.53 (1) Å. Each of the four shorter Cr···Cr diagonals is bridged by a single mhp ligand, bonded to one Cr atom through oxygen and to the other through nitrogen. This is the normal mode of bridging, as observed in the $[M_2(mhp)_4]$ complexes[2-8] and in $[Cu_4(mhp)_4]$,[10] but the span of 2.829 (1) Å in $[Cr_4(OH)_4(mhp)_8]$ is the longest so far observed for a bridging mhp ligand. It is interesting to note that the smallest metal–metal separation bridged by mhp is for the same metal, albeit in a different oxidation state and with a different metal–metal bond multiplicity; thus, the Cr–Cr separation in $[Cr_2(mhp)_4]$[2,3] is almost 1 Å shorter than that observed here.

Each of the remaining four mhp ligands is bonded through oxygen to one of the Cr atoms and forms a hydrogen bond with a μ_3-OH group, with a N···O distance of 2.57 (1) Å. The coordinates of this hydrogen atom were freely refined, but in view of the large esd values, it is not possible to assign the hydrogen atom unequivocally to either the oxygen or the nitrogen atom. These mhp ligands closely resemble the axial Hmhp ligand in $[Rh_2(mhp)_4(Hmhp)]$,[9] in which a hydrogen bond is formed between the nitrogen atom of the axial ligand and the oxygen atom of one of the bridging ligands, with a N···O distance of 2.74 (1) Å.

Each Cr atom is essentially octahedrally coordinated, with three Cr–OH, two Cr–O(mhp), and one Cr–N bonds. The central Cr_4O_4 core has a geometry similar to that in $[(\eta^5\text{-}C_5H_5)_4Cr_4O_4]$,[20] although the distortion is somewhat different because of the very different ligand arrangement.

Magnetic Properties. The electronic structure of $[Cr_4(OH)_4(mhp)_8]$ involves an antiferromagnetic spin-coupling regime among the four Cr(III) d^3 centers of the tetrameric unit. This interpretation is based on the room-temperature (298 K) magnetic moment of 3.18 μ_B per Cr atom, which is appreciably less than the value of 3.84 μ_B observed for simple $S = {}^3/_2$ paramagnets such as $Cr_2(SO_4)_3{\cdot}K_2SO_4{\cdot}24H_2O$ and $K_3[Cr(C_2O_4)_3]$. The EPR spectrum of powdered $[Cr_4(OH)_4(mhp)_8]$ at 300 K displays a broad (ca. 250 G peak-to-peak line width) isotropic signal, with $g = 1.943$, at X-band frequency. The appearance of a weak feature of apparent g value 4.003 in this spectrum is indicative of a ground state with $S > {}^1/_2$. The comparative temperature variation of the second integral of the EPR signal intensity per unit gain for $[Cr_4(OH)_4(mhp)_8]$, $Cr_2(SO_4)_3{\cdot}K_2SO_4{\cdot}24H_2O$, and $K_3[Cr(C_2O_4)_3]$ is displayed in Figure 3. The form of the decrease in the EPR signal intensity with decreasing temperature for $[Cr_4(OH)_4(mhp)_8]$ contrasts with that for the other two compounds and is also consistent with the presence of antiferromagnetic exchange interactions within the cluster.

$[(C_5H_5)_4Cr_4O_4]$ also apears to involve antiferromagnetic coupling between the metal centers, but no EPR signal could be observed for this cubane-like cluster.[20]

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Registry No. $[Cr_4(OH)_4(mhp)_8]$, 95693-74-6; $[Cr(CO)_6]$, 13007-92-6; $[Cr_2(mhp)_4]$, 67634-82-6.

Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Cluster Synthesis. 9. Importance of Triply Bridging Sulfido Ligands in the Synthesis of Mixed-Metal Clusters: Synthesis and Crystal and Molecular Structure of $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$

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Sulfido ligands have proven to be of great value for the synthesis of metal carbonyl cluster compounds.[2] Triply bridging sulfido ligands are particularly valuable because they contain a lone pair of electrons that can be used for donation to other unsaturated metal centers.[2-4] In our recent studies we have found that the compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) readily adds unsaturated metal-containing fragments to form higher nuclearity[5,6] and mixed-metal cluster[7,8] compounds. Structural studies have shown that metal–metal bond formation has played a prominent role in the formation of all of these complexes.

Table I. Crystallographic Data

General Data			
formula	$Os_3WS_2O_{14}C_{14}$		
space gp	$P2_1/c$	temp, °C	28
a, Å	13.716 (2)	V, Å^3	4719 (4)
b, Å	22.611 (9)	M_r	1210.7
c, Å	15.248 (4)	Z	8
β, deg	93.63 (2)	ρ_{calcd}, g/cm^3	3.41
Measurement of Intensity Data			
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)		
monochromator	graphite		
detector aperture, mm			
horiz ($A + B \tan \theta$)			
A	3.0		
B	1.0		
vert	4.0		
cryst faces	$1\bar{1}\bar{1}$, 211, $\bar{1}10$, 121, 120, 011, $02\bar{1}$		
cryst size, mm	0.15 × 0.15 × 0.15		
reflcns measd	$+h, +k, \pm l$		
max 2θ, deg	47		
scan type	moving crystal		
ω-scan width (A + 0.347 tan θ) A, deg	1.00		
bkgd	$^1/_4$ addnl at each end of scan		
ω-scan rate (variable), deg/min			
max	10.0		
min	1.4		
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	3345		
Treatment of Data			
abs cor			
coeff, cm^{-1}	213.3		
grid	8 × 8 × 14		
transmiss coeff			
max	0.14		
min	0.06		
p factor	0.03		
final residuals: R_F	0.055		
R_{wF}	0.059		
esd of unit wt observn	1.80		
largest shift/error value of final cycle	0.39		
largest peak in final diff Fourier, e$_0$/Å^3	2.02		

In this report we describe the synthesis and structural characterization of the compound $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**), which is formed when solutions of **1** and $W(CO)_6$ are exposed with UV radiation.

Experimental Section

$Os_3(CO)_9(\mu_3\text{-}S)_2$ was prepared as previously described.[9] $W(CO)_6$ was purchased from Strem Chemicals, Danvers, MA. UV irradiations were performed upon solutions in Pyrex glassware by using an external high-pressure mercury lamp. IR spectra were recorded on a Nicolet 5SX FT IR spectrophotometer.

Preparation of $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (2). A 0.042-g (0.05 mmol) portion of $Os_3(CO)_9(\mu_3\text{-}S)_2$ and 0.019 g (0.055 mmol) of $W(CO)_6$ were dissolved in 180 mL of hexane and the resultant mixture photolyzed for 45 min under an N_2 atmosphere. The yellow solution turned to orange-red. The solvent was removed in vacuo, and the residue was chromatographed on silica TLC plates. Elution with hexane/CH_2Cl_2 (90/10) separated the starting material (0.008 g) from the orange product $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**): 0.040 g, (70%); IR (ν(CO) in hexane) 2087 (s), 2072 (m), 2066 (s), 2024 (s), 2019 (sh), 1947 (s) cm^{-1}. Anal. Found (calcd): C, 14.27 (13.89); H, 0.17 (0.00).

Crystallographic Analysis. Dark orange crystals of **2** suitable for X-ray diffraction measurements were grown from hexane/methylene chloride solutions by slow evaporation of the solvent at 4 °C. The data crystal was mounted in thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated dif-

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