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Synthesis and Molecular Structure of $Ru_2(C_5NH_4NH)_6(PMe_2Ph)_2$, a Ru–Ru-Bonded Molecule with 2-Pyridinylamide Ligands in Three Coordination Modes and Other Novel Features

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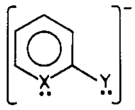
Received January 6, 1984

The title compound was obtained by reaction of $Ru_2(O_2CCH_3)_4Cl$ with the lithium salt of 2-aminopyridine, $Li(C_5NH_4NH)$, in tetrahydrofuran, followed by addition of PMe_2Ph. The dark red crystals formed on slow evaporation belong to the monoclinic system, space group $P2_1/c$, with unit cell dimensions of $a = 11.159$ (6) Å, $b = 10.067$ (6) Å, $c = 20.193$ (10) Å, $\beta = 82.97$ (4)°, $V = 2251$ (2) Å^3, and $Z = 2$. The molecule consists of two Ru atoms that have distorted-octahedral coordination united by a shared edge and a Ru–Ru bond. The anionic ligand, ap^-, exhibits three modes of coordination: (1) with the two ruthenium atoms bridged through N(py) and N(amine), (2) with the amine nitrogen as a bridging (μ,η^1) atom, and (3) with the amine nitrogen atom as a terminal ligand atom. The Ru–Ru distance is 2.573 (2) Å, the Ru–P distance is 2.388 (4) Å, and the Ru–N distances are in the range 2.05–2.13 Å. A Ru–Ru bond order of 1.0 based on a σ overlap is proposed and discussed. This is the first edge-sharing bioctahedral molecule having a bond between two d^5 metal atoms and also the first in which the (μ,η^1) bridging atoms are imido nitrogen atoms.

Introduction

It is recognized[1] that monoanionic bridging ligands of the related types **1** and **2** can have several modes of coordination, e.g., bridging of two metal centers through X and Y (**3**), bridging through either X or Y (**4**), chelation (**5**), and unidentate coordination (**6**). It is their suitability for the first mode that makes such ligands especially useful in forming stable, metal–metal-bonded species with many transition metals.[1] In the chemistry of ruthenium, however, the only structurally characterized compounds containing such ligands are $Ru_2(mhp)_4{\cdot}CH_2Cl_2$[2] and the carboxylates $Ru_2(O_2CCH_3)_4Cl$.[3] We thus turned our attention to the possibility of getting some additional dinuclear ruthenium species and chose the anion, ap^-, of 2-aminopyridine as a ligand. Our intention was to prepare the compound $Ru_2(ap)_4$, which would be similar to $Ru_2(mhp)_4{\cdot}CH_2Cl_2$. We were unsuccessful in doing this, but by changing the reaction conditions, we have isolated a novel compound, $Ru_2(ap)_6(PMe_2Ph)_2$, in which the ap^- ligand exhibits three different modes of coordination. The compound also contains a Ru–Ru bond and is thus the first example of a metal–metal-bonded species having aminopyridine as a bridging ligand. In an earlier report[4] it was shown that, in the case of Mo and W, 2-aminopyridine forms polymeric species that could not be isolated and characterized.



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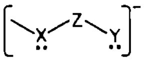

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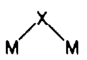

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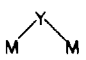

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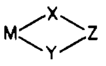

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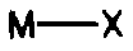

6a

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Experimental Section

Preparation of $Ru_2(ap)_6(PMe_2Ph)_2$ (1). $Ru_2(O_2CCH_3)_4Cl$ (0.12 g, 0.25 mmol), prepared by a literature method,[5] was suspended in 10 mL of tetrahydrofuran (THF). In another flask, under a dinitrogen atmosphere, 0.1 g (ca. 1 mmol) of 2-aminopyridine (Hap) was dissolved in 10 mL of THF. To this solution was added slowly with stirring 0.63 mL (1 mmol) of *n*-butyllithium (1.6 M in hexane). The solution of the lithium salt of 2-aminopyridine was then added to the flask containing $Ru_2(O_2CCH_3)_4Cl$. The mixture was stirred under an N_2 atmosphere at −20 °C for 1 h and then allowed to warm slowly to the room temperature, where it was stirred for an additional 12 h. The resulting solution was yellow-brown. To this solution was added slowly 0.08 g (0.58 mmol) of PMe_2Ph. After it was stirred for 1 h, the solution had become red-brown and appeared to be stable to air. The solution was then filtered, and 20 mL of hexane was added. On slow evaporation in air, dark red crystals suitable for x-ray diffraction were deposited. The crystals were only slightly soluble or insoluble in all solvents; yield ca. 40 mg, 15%.

X-ray Crystallographic Procedures. The structure of **1** was obtained by using the same general procedures as described elsewhere.[6,7] A

Table I. Crystallographic Data

formula	$Ru_2P_2N_{12}C_{46}H_{52}$
fw	1037.1
space group	$P2_1/c$ (No. 14)
systematic absences	$0k0$ ($k = 2n$), $h0l$ ($l = 2n$)
a, Å	11.159 (6)
b, Å	10.067 (6)
c, Å	20.193 (10)
β, deg	82.97 (4)
V, Å^3	2251.3 (2.1)
Z	2
d_{calcd}, g/cm^3	1.53
cryst size, mm	0.3 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	7.74
data collection instrument	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo
orientation reflcns: no., range (2θ)	No. 15, $17.4 < 2\theta < 26.0$
temp, °C	25
scan method	ω–2θ
data collecn range, 2θ, deg	5–50
no. of unique data, total with $F_o^2 > 2.5\sigma(F_o^2)$	1343, 1315
no. of parameters refined	235
R[a]	0.054
R_w[b]	0.072
quality-of-fit indicator[c]	1.544
largest shift/esd, final cycle	0.72
largest peak, e/Å^3	0.71

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
(2) Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112.
(3) See ref 1, pp 195–198.
(4) Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3541.
(5) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.

0020-1669/84/1323-4030$01.50/0

Table II. Positional Parameters and Their Estimated Standard Deviations in $Ru_2(ap)_6(PMe_2Ph)_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ru	−0.0102 (1)	0.0304 (1)	0.06233 (6)	1.89 (2)
P(1)	0.0969 (4)	0.1613 (4)	0.1344 (2)	2.8 (1)
N(A1)	−0.116 (1)	0.188 (1)	0.0385 (6)	2.7 (3)
N(P1)	0.086 (1)	−0.147 (1)	0.0767 (5)	2.4 (3)
N(A2)	−0.125 (1)	−0.016 (1)	0.1466 (5)	3.0 (3)
N(P2)	0.232 (1)	0.686 (1)	0.3286 (7)	4.1 (4)
N(A3)	0.134 (1)	0.072 (1)	−0.0105 (5)	1.7 (3)
N(P3)	0.305 (1)	0.175 (1)	−0.0615 (6)	3.2 (3)
C(1)	0.091 (2)	0.111 (2)	0.2240 (9)	4.3 (4)*
C(2)	0.048 (2)	0.335 (2)	0.1430 (8)	4.0 (4)*
C(11)	0.262 (1)	0.169 (2)	0.1115 (7)	2.8 (3)*
C(21)	0.854 (1)	0.287 (1)	0.4789 (7)	2.2 (3)*
C(31)	0.221 (1)	0.550 (2)	0.3209 (7)	5.6 (4)
C(41)	0.187 (1)	0.189 (2)	−0.0371 (7)	2.9 (4)
C(12)	0.317 (2)	0.286 (2)	0.0937 (9)	4.2 (4)*
C(13)	0.446 (2)	0.287 (2)	0.0743 (9)	4.7 (4)*
C(14)	0.486 (1)	0.671 (2)	0.4270 (8)	4.1 (4)*
C(15)	0.550 (2)	0.553 (2)	0.4085 (9)	4.5 (4)*
C(16)	0.673 (2)	0.551 (2)	0.3898 (9)	4.3 (4)*
C(22)	0.236 (1)	−0.309 (1)	0.0320 (8)	4.7 (4)
C(23)	0.257 (2)	0.651 (2)	0.0982 (8)	3.7 (4)
C(24)	0.183 (2)	0.706 (2)	0.1529 (8)	3.8 (4)
C(25)	0.105 (1)	−0.193 (1)	0.1395 (7)	5.0 (4)
C(32)	0.313 (1)	0.474 (2)	0.2769 (8)	7.5 (5)
C(33)	0.413 (2)	0.539 (2)	0.244 (1)	9.1 (6)
C(34)	0.424 (1)	0.680 (2)	0.2532 (9)	8.8 (6)
C(35)	0.673 (2)	0.248 (2)	0.2065 (9)	7.7 (5)
C(42)	0.125 (1)	0.312 (2)	−0.0400 (8)	5.7 (4)
C(43)	0.192 (2)	0.421 (2)	−0.0710 (9)	7.0 (5)
C(44)	0.686 (2)	0.596 (2)	0.0969 (9)	4.4 (5)
C(45)	0.633 (2)	0.720 (2)	0.0902 (9)	7.0 (5)

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material.

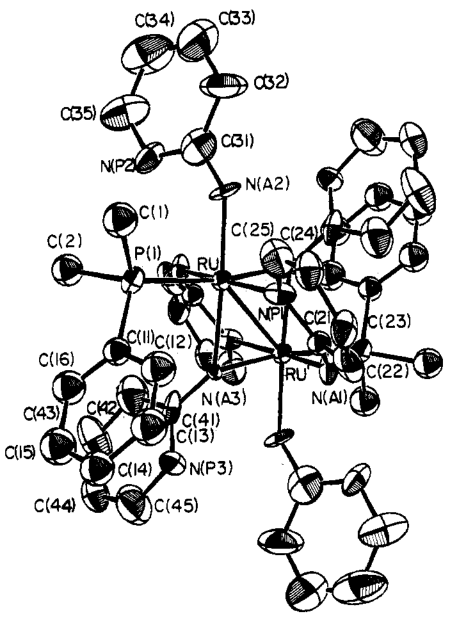

Figure 1. ORTEP drawing of the $Ru_2(ap)_6(PMe_2Ph)_2$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labeling scheme in this centrosymmetric molecule is defined.

Table III. Some Important Bond Distances (Å) in $Ru_2(ap)_6(PMe_2Ph)_2$ (1)

Ru-Ru	2.573 (2)	N(A1)-C(21)	1.310 (15)
-P(1)	2.388 (4)	N(P1)-C(21)	1.400 (15)
-N(A1)	2.073 (11)	-C(25)	1.388 (15)
-N(P1)	2.125 (11)	N(A2)-C(31)	1.36 (2)
-N(A2)	2.054 (9)	N(P2)-C(31)	1.39 (2)
-N(A3)	2.085 (9)	-C(35)	1.36 (2)
-N(A3)′	2.104 (9)	N(A3)-C(41)	1.40 (2)
P(1)-C(1)	1.871 (15)	N(P2)-C(41)	1.35 (2)
-C(2)	1.84 (2)	-C(45)	1.36 (2)
-C(11)	1.845 (13)		

Table IV. Some Important Bond Angles (deg) in $Ru_2(ap)_6(PMe_2Ph)_2$

Ru′-Ru-P(1)	137.4 (1)	Ru-P(1)-C(1)	118.7 (5)
-N(A1)′	86.6 (3)	-C(2)	114.9 (5)
-N(P1)	87.0 (3)	-C(11)	115.5 (5)
-N(A2)	136.7 (3)	C(1)-P(1)-C(2)	100.9 (7)
-N(A3)	52.4 (3)	-C(11)	99.7 (6)
Ru-Ru′-N(A3)	51.8 (3)	C(2)-P(1)-C(11)	104.8 (7)
P(1)-Ru-N(A1)	93.5 (3)	Ru′-N(A1)-C(21)	125.0 (9)
-N(P1)	94.7 (3)	Ru-N(P1)-C(21)	119.2 (8)
-N(A2)	85.8 (3)	Ru-N(P1)-C(25)	122.7 (9)
-N(A3)	85.3 (3)	N(A1)-C(21)-N(P1)	120 (1)
-N(A3)′	169.0 (3)	C(21)-N(P1)-C(25)	118 (1)
N(A1)′-Ru-N(P1)	171.7 (4)	Ru-N(A2)-C(31)	132 (1)
-N(A2)	92.8 (4)	N(A2)-C(31)-N(P2)	120 (1)
-N(A3)′	95.5 (4)	C(31)-N(P2)-C(35)	118 (2)
-N(A3)	80.3 (4)	Ru-N(A3)-Ru′	75.8 (3)
N(P1)-Ru-N(A2)	88.3 (4)	-C(41)	119.6 (8)
-N(A3)′	84.6 (4)	Ru′-N(A3)-C(41)	134.0 (9)
-N(A3)	91.6 (4)	Ru-N(A3)-C(42)	108.3 (5)
N(A2)-Ru-N(A3)	168.2 (4)	Ru′-N(A3)-C(42)	108.0 (5)
-N(A3)′	85.4 (4)	N(A3)-C(41)-N(P3)	113 (1)
N(A3)-Ru-N(A3)′	104.2 (3)	-C(42)	125 (1)

Results and Discussion

As noted in the Introduction, this work was undertaken with the goal of preparing a $Ru_2(ap)_4$ or $Ru_2(ap)_4^+$ species similar in general structure to the $Ru_2(mhp)_4$ molecule or the $Ru_2(O_2CR)_4^+$ species. While $Ru_2(O_2CCH_3)_4Cl$ reacted smoothly with the lithium salt of Hap in tetrahydrofuran, to give a yellow-brown solution that may well have contained a product of the desired type, all efforts to recover a clean crystalline product failed. With the idea of blocking the axial positions by bulky ligands so as to promote the formation of a crystalline product, the PMe_2Ph ligand was added. This promptly caused a change in the color of the solution to red-brown (not in itself necessarily a bad sign), and from this solution we obtained a dark red crystalline product. Unfortunately, once precipitated, this substance was virtually insoluble in THF or any other solvent and we have been unable to characterize it by NMR. The crystal structure, to be discussed in detail presently, shows that it is not a product of the anticipated type but instead a binuclear compound of ruthenium(III). The original Ru^{II}–Ru^{III} unit has thus been oxidized, but we are not able to say how. The reaction conditions are reducing in character, rather than oxidizing, but it must be remembered that the characterized product was formed in only about 15% yield, leaving open the possibility of disproportionation.[8]

The isolated product was shown by X-ray crystallography to consist of dinuclear molecules, $Ru_2(ap)_6(PMe_2Ph)_2$. The

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(6) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A*: *Cryst. Phys., Diffr., Theor. Gen Crystallogr.* **1968**, *A24*, 351.

(7) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with a VAX-SDP software package.

(8) A reviewer has suggested that oxidation may have occurred as crystals were grown from a solution exposed to air. This cannot be ruled out, but since the solution did not undergo any visible change on first exposure to air, or at any time thereafter, we do not favor this idea.

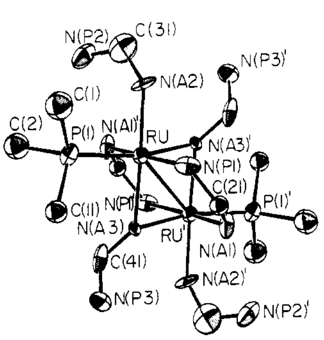

Figure 2. ORTEP drawing showing the three modes of coordination of the ap ligand. N(A) and N(P) are the amino and pyridine ring nitrogens, respectively. Symmetry-related atoms are designated by prime notation.

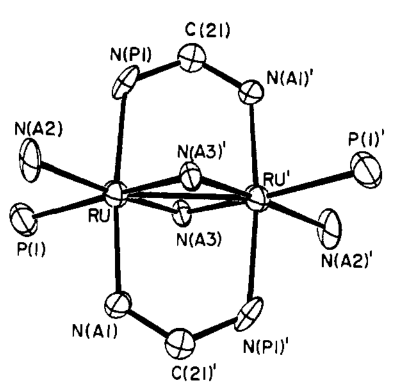

Figure 3. ORTEP drawing showing the common edge sharing by two octahedra.

atomic coordinates and equivalent isotropic thermal vibration parameters are listed in Table II. The structure of the molecule, which resides on a crystallographic center of inversion, is shown in Figure 1, which also gives the complete atom-labeling scheme. Important bond lengths and bond angles are listed in Tables III and IV. Complete lists are available as supplementary material.

The central portion of the structure is shown in Figure 2. From the point of view of ligand comportment, it is clear in this drawing that this molecule presents a novel (through not unique[9]) display of a given ligand, ap$^-$ in this case, engaged in three different modes of coordination in the same molecule. In one case, represented by the N(P1)–C(21)–N(A1) chain, the ap$^-$ ligand forms a three-atom bridge across two ruthenium atoms. This is the bonding mode we were hoping to get exclusively. The two kinds of Ru–N bonds to this ligand differ slightly in length, with the one to the neutral nitrogen atom, N(P1), being about 0.05 Å longer than the one to the amine nitrogen atom, N(A1). This is the relationship previously seen in the group 6 compounds containing the 6-methyl-2-aminopyridine ligand, M$_2$(map)$_4$.[4]

The second type of ap$^-$ ligand, represented by the N(P2)–C(31)–N(A2) chain, is a unidentate, terminal ligand, bound through the amino nitrogen atom, N(A2). This Ru–N bond is the shortest one, as might have been expected. The third type of ap$^-$ ligand, represented by N(P3)–C(41)–N(A3), has the amine nitrogen atom, N(A3), serving as a μ bridge. The Ru–N bridge bonds are symmetrical within experimental error since the apparent difference, 0.019 (13) Å, is not statistically significant.

The Ru–P distance, 2.388 (4) Å, is normal as are the various other distances found in this central portion of the molecule and listed in Table III.

Turning now to the overall structure of the molecule, it can be described as an edge-sharing bioctahedron with a metal-to-metal bond. The Ru–Ru distance is 2.573 (2) Å, and the angles in the central Ru(μ-N)$_2$Ru quadrilateral, 75.8 (3)° at the bridging nitrogen atoms and 104.2 (3)° at the ruthenium atoms, are indicative of an attractive force between the ruthenium atoms. There are a number of other small angular distortions from the ideal octahedral angles, 90 or 180°, about each metal atom. The edge-sharing bioctahedral structure is clearly evident in the view of the innermost core of the molecule presented in Figure 3. Edge-sharing bioctahedral molecules have been discussed from a theoretical point of view by Shaik, Hoffmann, Fisel, and Summerville,[10] who gave a broad overview of the entire class, and by Cotton, Walton, et al.,[11] who focused on the details of the d^2–d^2 case where a double bond is formed between the metal atoms. The present case is of special interest for several reasons: (1) it is only the second case where the bridging ligands are imido groups;[12,13] (2) it is the only case where there are two d^5 metal atoms forming a bond;[14] (3) it contains bidentate ligands that bridge the adjacent axial positions, which is rare, though not unprecedented. Because of these unique or special features, it is difficult to make informative comparisons with other molecules. Since the size of the μ,η^1 bridging atoms has a major effect on the ability of the metal atoms to interact with each other, it is important to choose cases where these are first-row atoms, rather than Cl or S.

Before turning to these comparisons, let us comment on the formulation of the electronic structure of Ru$_2$(ap)$_6$(PMe$_2$Ph)$_2$ that would be suggested by the earlier theoretical work.[10,11] After formation of all metal–ligand σ bonds, each Ru^{III} atom should have an electronic configuration that would be expressed as $t_{2g}{}^5$ in full octahedral symmetry. These t_{2g} (or dπ) octahedral orbitals on the two metal atoms can overlap to form σ-, π-, and δ-bonding orbitals along with the related σ^*, π^*, and δ^* orbitals. The exact ordering of all these levels is subject to some uncertainty, but it is clear that σ should be most stable and σ^* least stable. The 10 avalable electrons will occupy all of these except σ^*, giving a net Ru–Ru σ bond.

In 1973 the structure of the [Ru$_2$(NH$_3$)$_8$(μ-NH$_2$)$_2$]$^{4+}$ cation was reported.[12] This is isoelectronic and quasi-isostructural with the molecule reported here. It has a slightly longer Ru–Ru distance, 2.625 (1) Å, which may indicate that the bridging ligands spanning the adjacent axial positions are facilitating closer approach, as first proposed by Hoffmann et al.[10] Such groups provide axial ligation with minimal ligand–ligand repulsive forces and should foster closer M–M bonding than would an otherwise similar set of unidentate axial ligands. However, as indicated by the comparison of the Ru–Ru bond lengths in our compound, 2.573 (2) Å, and that in the [Ru$_2$(NH$_3$)$_8$(NH$_2$)$_2$]$^{4+}$ ion, 2.625 (1) Å, still another factor must be at work here.

Other molecules comparable to Ru$_2$(ap)$_6$(PMe$_2$Ph)$_2$ are some ditungsten(V) and dimolybdenum(V) molecules that contain bridging OR groups.[15-17] These molecules should have

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(9) To cite but one prior example, see: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603. In this work the W$_2$(O$_2$CNMe$_2$)$_6$ molecule is described in which two ligands bridge, two are chelating, and two are essentially unidentate.

(10) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

(11) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Ilsley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

(12) Flood, M. T.; Ziolo, R. F.; Early, J. E.; Gray, H. B. *Inorg. Chem.* **1973**, *12*, 2153.

(13) Bridging μ,η^1 nitrogen atoms of thiocyanate ions are also known in one case, [Re$_2$(NCS)$_{10}$]$^{3-}$. Cf.: Cotton, F. A.; Davison, A.; Ilsley, W. H.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 2719.

(14) The [Mn$_2$Cl$_6$(H$_2$O)$_4$]$^{2-}$ ion has an Mn···Mn distance of 3.83 Å, and the high-spin metal ions are only loosely coupled ($J = -0.015$ cm^{-1}). Cf.: Willett, R. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 178.

M–M σ bonds, and the bridging atoms are first-row atoms. However, the W–W and Mo–Mo bond lengths are in the range 2.69–2.73 Å, which are much longer than that found here. We believe that this difference can be attributed to one or, most likely, two factors, both of which have been discussed in connection with other M–M-bonded systems. One of these factors is the presence of two three-atom bridging groups.

Second, in the present ruthenium compound the formal oxidation number of the metal atoms is only +3 as compared to +5 in the tungsten and molybdenum compounds. As noted, and documented several times previously, in a variety of structural contexts,[18,19] an increase in the extent of ionization of the metal atoms causes a contraction of their d orbitals and this in turn causes poorer d–d overlap. Thus, we would argue that the d–d σ bond-forming potential of the Ru^{III}-Ru^{III} pair of atoms is appreciably greater than that of the W^{V}–W^{V} and Mo^{V}–Mo^{V} pairs and that this will also favor a shortening from ca. 2.70 to 2.57 Å on going from the M^{V}–M^{V} to the M^{III}–M^{III} case.

Acknowledgment. We thank the U. S. National Science Foundation for support.

Registry No. **1**, 92669-47-1; $Ru_2(O_2CCH_3)_4Cl$, 38833-34-0; Ru, 7440-18-8.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters, complete lists of bond distances and bond angles, and details of the crystal structure determination (16 pages). Ordering information is given on any current masthead page.

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New Preparative Methods, Structure, and Nitration of Bi-oxo-capped Trimolybdenum(IV) and Tritungsten(IV) Cluster Cations

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Received January 19, 1984

The reaction of $Mo_2(O_2CC_6H_5)_4$ with dibenzoyl peroxide (1:2 mole ratio) in methylene chloride, followed by ethanolic workup, leads to the $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ cation. The product has been isolated as the ClO_4^- salt, which has been characterized crystallographically. The compound forms triclinic crystals in the space group $P\bar{1}$ with a = 13.837 (3) Å, b = 22.189 (5) Å, c = 11.394 (3) Å, α = 92.39 (1)°, β = 114.35 (1)°, γ = 89.02 (1)°, V = 3185 (3) Å^3, and Z = 2. Important dimensions are $Mo\text{–}Mo_{av}$ = 2.761 [1] Å, $Mo\text{–}(\mu_3\text{-}O)_{av}$ = 1.983 [6] Å, $Mo\text{–}O(benzoate)_{av}$ = 2.081 [6] Å, and $Mo\text{–}O(H_2O)_{av}$ = 2.123 [6] Å. Cross experiments utilizing $Mo_2(OAc)_4$ and dibenzoyl peroxide suggest that the reaction mechanism may involve an initial oxidative addition to the metal–metal bond. The reaction between $W(CO)_6$ and benzoic acid at 160 °C followed by ethanolic workup yields the homologous $[W_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ cation. This product has been spectroscopically characterized. The remarkable chemical stability of each trinuclear unit is demonstrated by the nitration of each of the six benzoate rings in the meta position to give a virtually quantitative yield of the analogous hexanitro compounds, which have been characterized by NMR spectroscopy.

Introduction

A variety of synthetic routes for trinuclear bicapped clusters of the general formula $[M_3(\mu_3\text{-}O)_2(O_2CR)_6L_3]^{n+}$ (M = Mo, W),[2-10] has been developed over recent years. However, R has been restricted to a rather limited number of aliphatic hydrocarbons. The only bridging carboxylates recorded in the literature are the acetato,[2-8] propionato,[9,10] and pivalato[9] ligands. We have now found that the bi-oxo-capped trinuclear clusters with bridging benzoates can be prepared in excellent yields. For molybdenum this complex can be formed by the reaction of dimolybdenum tetrabenzoate ($M\overset{4}{-}M$) with 2 equiv of dibenzoyl peroxide. For the tungsten analogue a more conventional approach has been used. When a large excess of benzoic acid is reacted with $W(CO)_6$ in a melt reaction, the tungsten benzoate trimer is obtained. New evidence for the great stability of these $[M_3O_2(O_2CR)_6L_3]^{2+}$ units is afforded by the observation that under the strongly acidic conditions required for nitration of the aromatic rings, the trinuclear units remain intact and are converted to the hexa-*m*-nitro derivatives in greater than 90% isolated yield.

Experimental Section

Preparation of $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3CH_3CH_2OH$. A weighed amount of dibenzoyl peroxide (533 mg, 2.2 mmol) was added to a suspension of $Mo_2(O_2CC_6H_5)_4$ (676 mg, 1 mmol) in 30 mL of CH_2Cl_2. This mixture was then refluxed for 10 h under argon, during which time the color of the solution changed from yellow to green, temporarily to black, and finally to a deep burgundy. At this point several workup procedures were followed.

(A) The red material **1** can be precipitated by adding hexane to a filtered solution, followed by cooling it overnight. The compound thus obtained is soluble in most nonprotic organic solvents. All attempts to grow crystals led only to microcrystalline or amorphous material.

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