High-Nuclearity Clusters of Ruthenium. Synthesis and Crystal and Molecular Structure of $Ru_8(CO)_{17}(\eta\text{-tol})(\mu_4\text{-}S)_2$ (tol = Toluene)

Sir:

The synthesis of high-nuclearity metal carbonyl cluster compounds continues to be a topic of great interest.[1,2] Curiously, however, for the element ruthenium there are very few examples of such high nuclearity compounds.[3] Indeed, for this element there have been only two reports of cluster complexes that contain metal nuclearities higher than six.[4] Recently, we have been investigating the use of sulfido ligands for promoting cluster synthesis.[5] We have now synthesized the new sulfido ruthenium carbonyl cluster compound $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**) and have found that it appears to be a valuable reagent for the synthesis of higher nuclearity clusters of ruthenium.[6]

A solution containing 25 mg of **1** in 15 mL of toluene solvent was added dropwise to a refluxing solution of 13 mg of $Ru_3(CO)_{12}$ in toluene solvent over a period of 20 min. After the addition was completed, the solution was refluxed for an additional 20 min. After cooling, the solvent was removed in vacuo, and the residue was chromatographed by TLC on silica gel with a 7/3, v/v, hexane/CH_2Cl_2 solvent mixture. Three bands separated. In order of elution they were as follows: $Ru_3(CO)_{12}$, 8.7 mg; a black compound, **2**, 2.4 mg; a dark brown compound, **3**, 7.6 mg, which has been characterized as $Ru_8(CO)_{15}(\mu\text{-}CO)_2(\eta\text{-tol})(\mu_4\text{-}S)_2$ (tol = toluene), 26% yield.[8] Compound **3** was characterized by a single-crystal X-ray diffraction analysis.[9] An ORTEP drawing of the molecular structure of **3** is shown in Figure 1. An ORTEP drawing of **3** without the toluene and carbonyl ligands is shown in Figure 2. The cluster consists of eight ruthenium atoms with two quadruply bridging sulfido ligands.[10] The metal atoms are arranged in the form of two fused square pyramids in which the square bases are bridged by the sulfido ligands. The mode of fusion is unique.[11] The Ru(1)–Ru(5) bond is common to both square pyramids, but this bond serves as a basal edge of the Ru(1), Ru(2), Ru(3), Ru(5), Ru(7) pyramid and an apical-basel edge of the Ru(1), Ru(4), Ru(5), Ru(6), Ru(8) pyramid. They are linked further by a bond between Ru(2) and Ru(6). Although the range of Ru–Ru bond distances is considerable, 2.689 (2)–2.873 (2) Å, all would be regarded as single-bond lengths.[10] There are 17 carbonyl ligands distributed as shown in Figure 1. Two of these are bridging ligands that span the Ru(4)–Ru(6) and Ru(4)–Ru(8) bonds. One, C(62)–O(62), is a semibridging ligand. An η-toluene ligand is π-bonded to Ru(3). This exhibited a twofold rotational disorder as indicated by the presence of two half-weighted methyl groups.

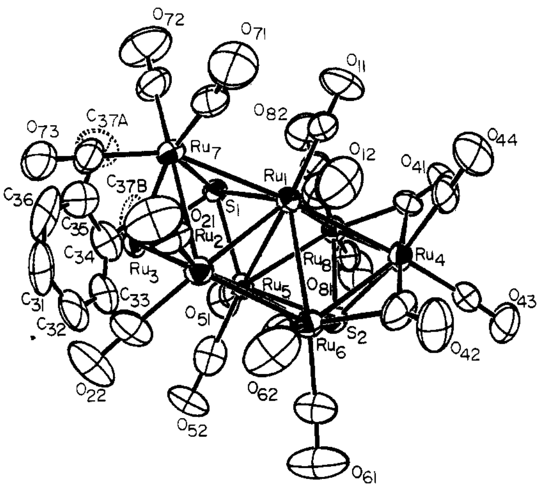

Figure 1. ORTEP diagram of $Ru_8(CO)_{15}(\mu\text{-}CO)_2(\eta\text{-tol})(\mu_4\text{-}S)_2$ (**3**), showing 50% probability thermal ellipsoids and the disordered methyl group on the toluene ligand.

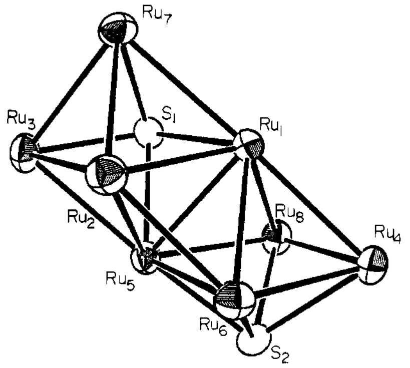

Figure 2. ORTEP diagram of **3** showing only the metal cluster and the sulfido ligands.

The cluster contains a total of 112 valence electrons. This number is in accord with predictions of the polyhedral skeletal electron pair theory as extended for applications to condensed polyhedra.[12] By this approach the cluster of **3** would be viewed as a square pyramid (74 electrons) fused to a capped square pyramid (86 electrons) through a triangular face (−48 electrons).

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(6) $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ can be prepared in 67% yield by the reaction of $Ru_3(CO)_{12}$ with C_2H_4S in refluxing hexane for 30 min. It can be isolated by TLC on silica gel by using hexane solvent in air. IR (ν(CO), cm^{-1}): 2075 vs, 2037 s, 2022 w, 1735 w. A prolonged reaction leads to the formation of $Ru_3(CO)_9(\mu_3\text{-}S)_2$. Details of these syntheses have been submitted for publication.[7]

(7) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.*, companion article in this issue.

(8) Compound **2** has not been completely characterized yet. Its IR spectrum is as follows: (ν(CO), cm^{-1}, hexane): 2083 vs, 2060 w, 2041 m, 2033 vw, 2029 vw. IR for compound **3** (ν(CO), cm^{-1}, hexane): 2077 w, 2054 vs, 2035 s, 2025 vs, 2017 m, 2010 w, 2002 w, sh, 1997 w, 1983 w, 1876 vw, 1852 vw. For **3** ^1H NMR (δ, 95% $CDCl_3$/5% C_6D_6): 7.16 (t, 1 H, J = 5.81 Hz), 6.49 (t, 2 H, J = 5.81 Hz), 6.39 (t, 1 H, J = 5.81 Hz), 5.66 (d, 1 H, J = 5.60 Hz), 2.15 (s, 3 H). A satisfactory elemental analysis has been obtained. From the baseline of the TLC 7.8 mg of $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$ was subsequently eluted with THF.[7]

(9) Dark brown block-shaped crystals of **3** were grown by slow evaporation of solvent from benzene solutions at 25 °C. The crystals belong to the monoclinic crystal system, space group $P2_1/n$, with a = 11.244 (4) Å, b = 20.344 (8) Å, c = 16.750 (5) Å, β = 92.28 (3)°, Z = 4 and ρ_{calcd} = 2.50 g/cm^3. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation at 23 °C. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX I computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption. The structure was solved by direct methods (MULTAN) and was refined (3947 reflections) to the final values of the residuals R = 0.045 and R_w = 0.051. The crystal was found to contain 0.5 mol of benzene solvent that had cocrystallized with each mole of complex.

(10) Selected interatomic distances (Å) for **3** are as follows (esd Ru–Ru = 0.002 Å): Ru(1)–Ru(2) = 2.739, Ru(1)–Ru(4) = 2.862, Ru(1)–Ru(5) = 2.739, Ru(1)–Ru(6) = 2.855, Ru(1)–Ru(7) = 2.873, Ru(1)–Ru(8) = 2.867, Ru(2)–Ru(3) = 2.769, Ru(2)–Ru(5) = 2.791, Ru(2)–Ru(6) = 2.689, Ru(2)–Ru(7) = 2.735, Ru(3)–Ru(5) = 2.791, Ru(3)–Ru(7) = 2.750, Ru(4)–Ru(6) = 2.752, Ru(4)–Ru(8) = 2.749, Ru(5)–Ru(6), = 2.808, Ru(5)–Ru(8) = 2.843, Ru(1)–S(1) = 2.401 (4), Ru(3)–S(1) = 2.348 (4), Ru(5)–S(1) = 2.395 (3), Ru(7)–S(1) = 2.451 (4), Ru(4)–S(2) = 2.470 (4), Ru(5)–S(2) = 2.391 (4), Ru(6)–S(2) = 2.403 (4), Ru(8)–S(2) = 2.398 (4).

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It is believed that the great paucity of high-nuclearity clusters of ruthenium may be due to the lack of suitable reagents and synthetic routes. The compounds **1** and $Ru_3(CO)_9(\mu_3\text{-}S)_2$, which we have made in good yield, may now permit the development of the area of sulfido ruthenium carbonyl cluster chemistry that may be as rich and varied as that of osmium.[5]

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Supplementary Material Available: Tables of crystal data, fractional atomic coordinates and thermal parameters, interatomic distances, selected interatomic angles, and anisotropic thermal parameters (16 pages); a table of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

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Monomeric Octahedral Cobalt(III) Complex of a Substituted *N*,*N*′-Bis(salicylidene)diethylenetriamine Ligand

Sir:

The first mononuclear octahedral complex of a transition metal with a H_2saldien-type ligand has been characterized by an X-ray crystal structure. Several investigators had concluded that octahedral complexes of H_2saldien, 2,2′-[iminobis(2,1-ethanediylnitrilomethylidyne)]bisphenol, could not exist because of steric constraints.[1–4] This conclusion probably originated from the statement that "similar difficulties would be encountered in its coordination through all five donor atoms to a single metal ion."[2] The misconception was reinforced by the coordination of saldien^{2-} in a planar arangement around the UO_2^{2+} ion[3] and the distorted-trigonal-bipyramidal dimers found in Cu(saldien).[4] The Ni(saldien) complexes were postulated as square planar with the central NH not coordinating.[5] Fe(saldien)[6] was considered to be either a tetracoordinated monomer similar to Ni(saldien)[5] or more likely a pentacoordinated dimer like Cu(saldien).[4] Recent interest in manganese complexes has stimulated new investigations into H_2saldien and other polydentate Schiff base ligands.[7] A dimeric octahedral structure for the Mn(saldien) complex was proposed.[7] In contrast our results demonstrate that H_2saldien and the various substituted derivatives can form monomeric octahedral complexes and that the ligand can indeed coordinate all five donor atoms to a single metal ion.

Substituted 2,6-diformylphenols have been used as starting materials for the synthesis of a large variety of binuclear metal complexes.[8–10] A precipitate was formed during an attempt to prepare a binuclear cobalt–europium complex via a template type reaction. Recrystallization of the solid from pyridine was unsuccessful. However, slow evaporation of a methanol–water solution of the pyridine-treated solid gave dark brown crystals suitable for an X-ray study.[11]

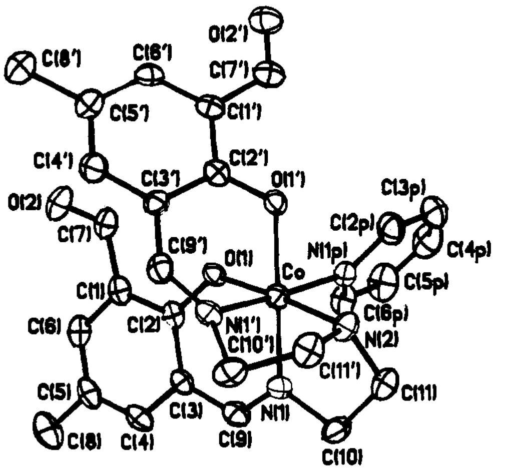

Figure 1. Structure of the Co(3-formyl-5-Me-saldien)(py)$^+$ cation showing 30% probability thermal ellipsoids. Bond lengths (Å) and angles (deg): Co–O(1) = 1.885 (4), Co–O(1′) = 1.896 (4), Co–N(1) = 1.906 (6), Co–N(1′) = 1.903 (5), Co–N(2) = 1.977 (5), Co–N(1p) = 1.972 (6); O(1)–Co–O(1′) = 86.1 (2), O(1)–Co–N(1) = 92.9 (2), O(1)–Co–N(1′) = 92.8 (2), O(1)–Co–N(1p) = 90.0 (2), O(1′)–Co–N(1p) = 87.4 (2), O(1′)–Co–N(2) = 97.2 (2), O(1′)–Co–N(1′) = 88.2 (2), N(1p)–Co–N(1) = 91.7 (2), N(1p)–Co–N(2) = 93.2 (2), N(1)–Co–N(1′) = 92.8 (2), N(2)–Co–N(1′) = 84.3 (2), N(1)–Co–N(2) = 83.8 (2).

The cation, with the atomic numbering, is illustrated in Figure 1. The octahedral arrangement around the central cobalt(III) ion is easily seen. The retention of the coordinated pyridine is surprising since the compound was recrystallized from methanol–water. Adducts of saldien complexes are apparently very stable. A pyridine adduct of Ni(5-Br-saldien) retained pyridine on being heated to 100 °C at reduced pressure.[5] The CH_3OH adduct of Mn(5-NO_2-saldien) lost only 10–20% of the methanol after being heated under vacuum at temperatures from 80 to 160 °C.[7] In view of our results the adducts of both the Ni and Mn complexes are probably monomeric octahedral structures.

The crystal structure of three cobalt saldpt complexes (saldpt is *N*,*N*′-bis(salicylidene)dipropylenetriamine) have been reported.[12–14] One of the complexes has a trans arrangement of the oxygen atoms,[12] but the other two have a cis arrangement similar to that of our complex.[13,14] The Co–O distances in the three complexes average 1.901 (14) Å, in agreement with our values. The central nitrogen of the ligand always has the longest Co–N distance [average 1.997 (33) Å], either a steric or hybridization effect. The Co–N distance to the C=N group [average 1.934 (16) Å] is slightly longer than our values. In general the dif-

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(11) The dark brown lathlike crystals are triclinic (space group $P\bar{1}$) with a = 10.121 (3) Å, b = 11.483 (3) Å, c = 14.047 (4) Å, α = 69.43 (2)°, β = 73.47 (2)°, γ = 79.47 (2)°, and V = 1459.0(7) Å^3. With two molecules of $[Co(C_{22}H_{23}N_3O_4)(C_5H_5N)]^+NO_3^-\cdot 2H_2O$, M_r = 629.55, D_x = 1.44 g cm^{-3}, D_m = 1.44 g cm^{-3}, and μ(Mo Kα) = 6.8 cm^{-1}. All measurements were made at room temperature, 27 °C, on a Nicolet R3m diffractometer with graphite-monochromatized Mo Kα radiation, λ = 0.71069 Å. The intensity crystal was 0.07 × 0.14 × 0.34 mm so that no absorption corrections were deemed necessary. A total of 4155 measurements were made in the 2θ range of 1.0–45.0° (hkl limits were 0–10, ±11, and ±15, respectively) by using a variable speed (2.0–29.3° mm^{-1}) ω-scan technique. After merging, 3808 unique reflections remained of which the 2792 with $F > 3\sigma(F)$ were used in the analysis. The cobalt atom was located by direct methods and the remaining atoms in successive Fourier syntheses. Refinement including an isotropic extinction factor was by least-squares methods to an R of 0.067 and R_w of 0.046. Only 26 of the H atoms were found in the difference Fourier synthesis with the remaining eight located by geometrical considerations. All calculations were carried out by using the programs, scattering factors, and other data incorporated in the DESKTOP SHELXTL system.

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