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]

Acknowledgment. This research was supported by the National Science Foundation under Grant No. CHE-8416460.

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]

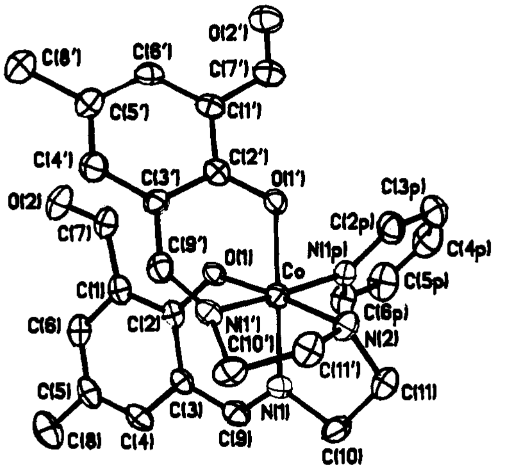

Figure 1. Structure of the Co(3-formyl-5-Me-saldien)(py)$^+$ cation showing 30% probability thermal ellipsoids. Bond lengths (Å) and angles (deg): Co–O(1) = 1.885 (4), Co–O(1') = 1.896 (4), Co–N(1) = 1.906 (6), Co–N(1') = 1.903 (5), Co–N(2) = 1.977 (5), Co–N(1p) = 1.972 (6); O(1)–Co–O(1') = 86.1 (2), 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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ferences in bond lengths between the saldpt complexes and our saldien complex are small at best. Sterically, the saldpt and saldien appear to be very similar with bond angles close to 90° and 180° as expected. Consequently, the difference in the chemical behavior of saldpt vs. saldien complexes is difficult to explain. One explanation may involve the tenacity of the sixth ligand in the saldien complexes compared to those of saldpt. The more rigid nature of saldien may provide a barrier to easy substitution of the sixth group, which would have a pronounced effect on the chemistry of saldien complexes. We are currently reexamining the chemistry of saldien complexes, particularly the cobalt case, with this concept in mind.

Acknowledgment. We thank the NSF Instrumentation Program for a grant for the purchase of the Nicolet diffractometer.

Supplementary Material Available: Tables of the final positional and thermal parameters, distances and angles, and hydrogen atom parameters (5 pages); a table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Articles

Contribution from Laboratoire de spectrochimie du solide and Laboratoire de chimie des polymères inorganiques, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

ENDOR Study of a One-Electron 2:18 Reduced Fluoropolytungstate

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One-electron electrochemical reduction of the $(H_2W_{18}F_6O_{56})^{8-}$ polyanion led to a mixed-valence compound. Electron trapping has been studied by fluorine and proton ENDOR spectroscopy using W^V as a probe. ^{19}F ENDOR has shown that the unpaired electron is trapped inside the equatorial rings of the 2:18 structure. ^1H ENDOR has shown that the WO_5F polyhedron is not strongly solvated.

Introduction

Fluoropolytungstates have recently been reported.[1-4] One of them $(H_2W_{18}F_6O_{56})^{8-}$[2] belongs to the 2:18 series, the structure of which was described by Dawson.[5] This polyanion is composed of two XW_9O_{39} subunits that can be derived from the well-known Keggin structure[6] by removing one WO_6 octahedron from three different edge sharing W_3O_{13} groups (Figure 1).

Two basic WO_6 units can be distinguished in such polyanion, those belonging to W_3O_{13} caps and those belonging to equatorial belts.

^1H and ^{19}F NMR experiments performed[2] on $(H_2W_{18}F_6O_{56})^{8-}$ have shown that the six fluorine atoms are distributed in two groups with three fluorine located at the corners of the two tetrahedral cavities surrounding the hydrogen atoms. Two sets of tungsten sites arise from such a structure, those WO_6 situated at the caps of the polyanion and those WO_5F situated at the equatorial belts.

Like other polyanions, these fluoropolytungstates can be electrochemically reduced,[8] leading to a mixed valence compound. We recently used ESR and optical spectroscopy[8] to study the electron delocalization process in the one-electron-reduced $(H_2W_{18}F_6O_{56})^{9-}$ compound.

The problem of electron trapping in the 2:18 structure is not yet clearly understood. Previous work[9] suggested that it should be trapped on one of the equatorial rings, i.e. on the WO_5F octahedron of the fluoropolytungstate unit $((H_2W_{18}F_6O_{56})^{8-})$. However our ESR experiments[8] did not reveal any superhyperfine coupling with ^{19}F nuclei even at very low temperature.

The aim of the present paper was to extend the characterization of the reduced polyanion $(H_2W_{18}F_6O_{56})^{9-}$ by using ENDOR spectroscopy. This approach provides a much better resolution than is available with ESR.

Experimental Section

$(H_2W_{18}F_6O_{56})^{8-}$ fluoropolytungstate was prepared according to a procedure previously described.[1] The purity of this polyanion was determined by ^{19}F NMR and chemical analysis.[2] Electrochemical reduction was performed under an argon atmosphere with a mercury cathode. The imposed potential (−150 mV vs. SCE) was given by a Tacussel PRT 500 LC. The reduction of the 10^{-1} M solution (HCl 0.1 M, NaCl 1 M) was followed by coulometry using an IG5N integrator.

ESR and ENDOR spectra were recorded on a Bruker ER 220D ESR spectrometer equipped with the Aspect 2000 computer-monitored ENDOR unit. The maximum rf power in the ENDOR coil was 100 W. The modulation scheme employed was frequency modulation of the radiofrequency. All experiments were carried out at temperatures between 4 and 10 K produced by using a helium-flow cryostat ESR 9 from Oxford Instrument. The maximum ENDOR enhancement was obtained by using an hf power of 2 mW and the maximum rf power available. The 10^{-1} M solution was merely frozen at these temperatures, without glass-forming additives.

Results and Discussion

The ESR of a frozen solution at 4 K of the one-electron-reduced $(H_2W_{18}F_6O_{56})^{9-}$ polyanion is shown in Figure 2a. This spectrum

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