

G in Me₂SO solution. A corresponding compound has now been isolated in crystalline form and is currently being examined. More information concerning the possible biological relevance for a platinum-caused base-mispairing mechanism might be expected from this compound.

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Supplementary Material Available: Listings of temperature factors, hydrogen-bonding distances, least-squares planes and dihedral angles, and moduli of F_o and F_c (49 pages). Ordering information is given on any current masthead page.

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Ketoximate Complexes. Structural and Spectroscopic Study of Tris(5,5-dimethylcyclohexane-1,2,3-trione 2-oximate)cobalt(III) and -ruthenate(II)

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The complexes Co(dmho)₃ and H[Ru(dmho)₃] have been isolated and characterized by UV-visible, infrared, and ¹H and ¹³C NMR spectroscopy (dmho⁻ is the monoanion of 5,5-dimethylcyclohexane-1,2,3-trione 2-oxime). The crystal and molecular structure of Co(dmho)₃ has been investigated by X-ray diffraction techniques. The compound crystallizes in the orthorhombic space group *P*2₁2₁2₁ with four molecules in the unit cell of dimensions *a* = 11.96 (1), *b* = 18.85 (2), and *c* = 11.89 (1) Å. The structure was solved by using 1207 symmetry-independent reflections. Refinement by full-matrix least-squares methods with anisotropic temperature factors for all nonhydrogen atoms gave a final *R* factor of 0.043. The neutral complex Co(dmho)₃ has spontaneously resolved upon crystallization to the *fac*- Δ isomer. The coordination polyhedron around cobalt is practically an octahedron with oxygen and nitrogen atoms disposed on opposite triangular faces in a facial configuration. The three five-membered chelate rings have been found to be strictly planar. The cyclohexane rings are puckered and adopt a δ' or λ' conformation. The crystal for which the structure was determined contains one *fac*- $\Delta(\lambda'\lambda'\delta')$ isomer. ¹H and ¹³C NMR measurements have been done on Co(dmho)₃ and H[Ru(dmho)₃]. The comparison of the spectra obtained by application of gated-decoupling techniques allows assignments of most resonances to individual carbons. It is found that ¹H and ¹³C NMR results agree with a facial configuration of the tris chelates in solution. However, there is no conformational preference for the cyclohexane rings in solution.

The current interest in complexes of transition metals with ketoxime^{2,3} and nitrosophenol⁴ ligands as potential models for metal binding sites in feroverdin^{5,6} has prompted the investigation of the structures and the overall coordination geometry of the metal center in these complexes.^{7,8} A further feature of interest is the role played by the (ketoximate)ruthenium complexes in the activation of nitrogen monoxide.^{10,11} Oximes and nitroso derivatives^{12,13} are interesting ligands since they have low-lying π^* systems which may be accessible for back-bonding and there is a possible ambiguity with regard to the site of binding at N or O atoms.¹⁴⁻¹⁸ More particularly

the ketoximes were found to chelate to transition metals through the N (oxime) and O (ketone) atoms.^{7-9,19-21} However, monodentate coordination via only one O or N atom has been reported.^{10,22} In view of the general interest in the factors determining the geometries and structures of ketoximate complexes, we have investigated the structure of Co(dmho)₃ (dmho⁻ is the monoanion of 5,5-dimethylcyclohexane-1,2,3-trione 2-oxime) to establish the absolute configuration of one diastereoisomer in the solid state. The ¹H and ¹³C NMR spectra are used as means of investigation of the stereochemistries of Co(dmho)₃ and [Ru(dmho)₃]⁻ in solution.

Experimental Section

Reagent grade materials dimedone, C₈O₂H₁₁ (5,5-dimethyl-1,3-cyclohexanedione), and Na₃[Co(NO₂)₆] were used as purchased; Na₂[Ru(NO)(NO₂)₄OH]·2H₂O was prepared by a previous procedure.²³ The elemental analyses were performed by the Microanalytical Laboratory of CNRS, Villeurbanne, France.

1. Co(O₃C₈H₁₀N)₃. A 4.3-g quantity (1.07 × 10⁻² mol) of Na₃[Co(NO₂)₆] is dissolved in 150 mL of water, and 4.48 g (3.2 × 10⁻²

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mol) of dimedone, $C_8O_2H_{12}$, is introduced into the solution. The solution is stirred and maintained at 50 °C for 24 h. After the solution cools to room temperature, the red precipitate is collected by filtration and washed with water. The compound is readily recrystallized as dark red crystals from an acetone–water mixture; yield 90%. Anal. Calcd for $CoO_9C_{24}H_{30}N_3$: C, 51.16; H, 5.33; N, 7.46; Co, 10.47. Found: C, 50.7; H, 5.3; N, 7.5; Co, 10.1.

2. $H[Ru(O_2C_8H_{10}N)_3]$. A 1-g quantity (2.5×10^{-3} mol) of $Na_2[Ru(NO)(NO_2)_4OH]$ is dissolved in 100 mL of water, and 2.1 g (1.5×10^{-2} mol) of dimedone is introduced into the solution. The pH of the solution is fixed at pH 3 with HCl. The solution is maintained at 40 °C for 12 h. After the solution cools, the pH is fixed at pH 1 with HCl. Secondary products are extracted with diethyl ether. Slow evaporation of the dark red aqueous solution slowly gives a microcrystalline dark red solid. The solid is collected by filtration, washed with cold methanol and diethyl ether, and dried in a vacuum desiccator over P_2O_5 ; yield 70%. Anal. Calcd for $RuO_9C_{24}H_{31}N_3$: C, 47.52; H, 5.1; N, 6.93; Ru, 16.67. Found: C, 46.8; H, 5.2; N, 7.0; Ru, 16.4.

Physical Measurements. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were obtained on a Beckman IR 12 spectrometer with KBr plates. UV–visible spectra were run on a Jobin-Yvon Duospac 203 instrument. The potentiometric data were obtained on a Radiometer PM 52 instrument with a glass electrode–solution–KCl (saturated solution)–calomel electrode system.

The 1H NMR spectra were taken on a Bruker WP 80 instrument operating in the Fourier transform mode at 37 °C unless otherwise indicated. Chemical shifts (δ) are reported in ppm relative to internal $(CH_3)_4Si$ in $CDCl_3$ or $(CD_3)_2SO$ solvent. The proton-noise-decoupled ^{13}C NMR spectra were recorded at 20.15 MHz on the same instrument. Typical parameters were as follows: pulse width 6 μs (i.e., 60° flip angle on spectrometer); no interpulse delay; acquisition time 0.8–1.6 s depending on the sweep width (5000 Hz) and number of data points (8 or 16 K). So that the signal to noise ratio of the quaternary carbon resonances could be optimized, a 3- μs pulse width (i.e., 30° flip angle) was also used. Usually 20 000–30 000 accumulations were necessary to achieve a satisfactory signal to noise ratio. The samples were contained in 10 mm o.d. tubes and were neither degassed nor sealed. The complexes were dissolved in $CDCl_3$ or $(CD_3)_2SO$ (0.2 M). Chemical shifts (δ) are reported in ppm relative to internal $(CH_3)_4Si$.

Proton-coupled spectra were obtained by the gated-decoupling technique (decoupler off only during acquisition). The parameters were 60° flip angle, 4.6-s pulse interval, a spectral width of 5000 Hz, and 16K data points.

Crystal Data. A well-formed dark red parallelepipedic crystal was mounted with one edge approximately parallel to the fiber axis and examined by the Weissenberg method with $Cu\ K\alpha$ radiation. Orthorhombic diffraction symmetry with the systematic absences of $h = 2n + 1$, $k = 2n + 1$, and $l = 2n + 1$ for, respectively, $h00$, $0k0$, and $00l$ reflections was observed and the space group $P2_12_12_1$ thereby deduced.

The unit cell dimensions ($a = 11.96$ (1), $b = 18.85$ (2), $c = 11.89$ (1) Å) were obtained from a least-squares refinement against the setting angles of 25 reflections on a Philips PW 1100 diffractometer with graphite-monochromated $Mo\ K\alpha$ radiation. There are four $Co(O_3C_8H_{10}N)_3$ units in the unit cell, giving a calculated density of 1.40 g/cm³ compared with the flotation density of 1.39 g/cm³. The θ – 2θ scan technique was used to record the intensities for all non-equivalent reflections for $2^\circ < \theta < 20^\circ$. The intensities of three standard reflections, monitored at 2-h intervals, showed no significant fluctuations. The raw intensity data were corrected for Lorentz–polarization effects. Absorption corrections based on the crystal dimensions (distances in mm of faces from centroid) 0.110 (010), 0.110 (0 $\bar{1}$ 0), 0.110 (101), 0.110 ($1\bar{0}$ 1), 0.083 (10 $\bar{1}$), and 0.083 ($1\bar{0}$ 1) were also applied ($\mu = 7.5\text{ cm}^{-1}$). The range of transmission factors was 0.85–0.87. Of the 1479 independent intensities, there were 1207 with $F_o^2 > 3\sigma(F_o^2)$. $\sigma(F_o^2)$ was estimated from counting statistics. These data were used in the refinement of the structural parameters.

Structure Solution and Refinement. The structure was solved by standard heavy-atom procedures and then refined by full-matrix least-squares methods.²⁰ Atom scattering factors²⁴ (ionic for Co(III) and neutral for C, N, O, and H) were used, and the real ($\Delta f'$) and

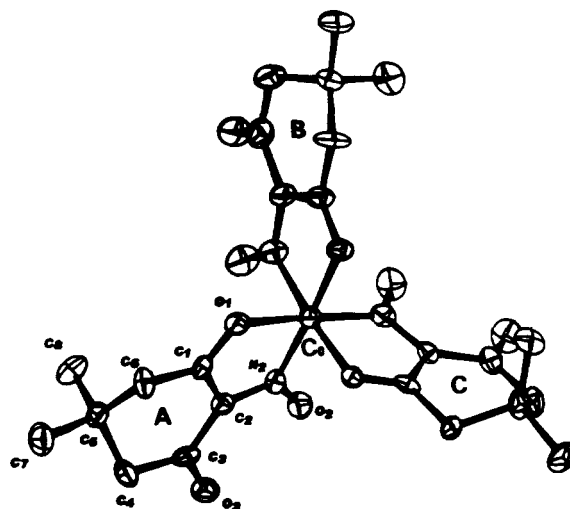


Figure 1. ORTEP drawing of the neutral complex tris(5,5-dimethylcyclohexane-1,2,3-trione 2-oximate)cobalt viewed down the pseudo-threefold axis. The individual atoms are drawn at 30% probability contours of the thermal motion. Hydrogen atoms are omitted.

imaginary ($\Delta f''$) corrections due to anomalous dispersion²⁵ were applied to the Co, C, N, O atom scattering function. Anisotropic thermal parameters for all nonhydrogen atoms were introduced, and the model converged with $R = 0.048$ and $R_w = 0.051$. At this point the sign of the imaginary component ($\Delta f''$) of the anomalous scattering correction of all atoms was reversed prior to an additional cycle of refinement to determine whether the correct enantiomorph had been selected. The error indices R and R_w decreased significantly to 0.043 and 0.046, respectively, implying that the appropriate isomer had now been chosen.

Results and Discussion

$Co(dmho)_3$ and $H[Ru(dmho)_3]$ have been prepared via the C_2 oximation of 5,5-dimethylcyclohexane-1,3-dione (dmh) by, respectively, $[Co(NO_2)_6]^{3-}$ and $[Ru(NO)(NO_2)_4OH]^{2-}$. The detailed analysis of the latter reaction mechanism has been reported in a recent paper.²⁶ Attempts to synthesize the compounds by the direct interaction of cobalt and ruthenium compounds with the free ligand $dmho^-$ (monoanion of 5,5-dimethylcyclohexane-1,3-dione 2-oxime) failed because of the instability of $dmho^-$.

Although the infrared spectra of $Co(dmho)_3$ and $H[Ru(dmho)_3]$ exhibit some differences, they present sufficient analogous features to allow the assumption of the same coordination for both Co and Ru in the solid state. It is noteworthy that in the 4000–650- cm^{-1} region, the spectra of the two complexes do not display more bands than the spectrum of the corresponding free ligand $dmho^-$, isolated as its barium salt. Frequency shifts of some characteristic bands occur upon coordination. In particular the strong band at 1620 cm^{-1} for free $dmho^-$ shifts to 1540 cm^{-1} for $Co(dmho)_3$ and to 1520 cm^{-1} for $H[Ru(dmho)_3]$. This band is assigned to a $\nu(C_1 = O_1)$ vibration. Absorptions near 1380 and 1300 cm^{-1} for the two complexes can be assigned to $\nu(C_2=N_2)$ and $\nu(N_2-O_2)$ by comparison with other works on ketoximate^{10,27,28} and nitroso¹² complexes. The UV–visible spectrum of $Co(dmho)_3$ in $CHCl_3$ exhibits two intense bands at 270 (ϵ 28 000) and 375 nm (ϵ 15 000) with a shoulder at ca. 470 nm. The UV–visible spectrum of $H[Ru(dmho)_3]$ in aqueous solution exhibits two intense bands at 300 (ϵ 36 000) and 470 nm (ϵ 18 000). The

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Table I. Fractional Atomic Coordinates^a

atoms	x ^a	y	z
Co	0.56256 (013)	0.50563 (008)	0.37841 (012)
Ligand A			
N(2)	0.6578 (08)	0.5532 (05)	0.2784 (09)
O(2)	0.6247 (07)	0.5884 (04)	0.1967 (08)
C(2)	0.7661 (11)	0.5484 (06)	0.3065 (10)
C(3)	0.8614 (11)	0.5824 (06)	0.2522 (10)
O(3)	0.8477 (07)	0.6257 (04)	0.1753 (07)
C(4)	0.9805 (10)	0.5691 (07)	0.3016 (13)
C(5)	0.9877 (09)	0.4953 (07)	0.3603 (10)
C(8)	0.9791 (13)	0.4358 (07)	0.2649 (13)
C(7)	0.1077 (11)	0.4921 (10)	0.4159 (13)
C(6)	0.8962 (09)	0.4883 (08)	0.4488 (09)
C(1)	0.7831 (10)	0.5018 (07)	0.4034 (08)
O(1)	0.6976 (07)	0.4758 (04)	0.4500 (06)
Ligand B			
N(2)	0.5588 (10)	0.4200 (5)	0.2959 (09)
O(2)	0.6030 (10)	0.4116 (5)	0.2049 (09)
C(2)	0.5046 (11)	0.3681 (6)	0.3518 (10)
C(3)	0.4861 (12)	0.2945 (7)	0.3119 (14)
O(3)	0.5133 (09)	0.2776 (5)	0.2163 (10)
C(4)	0.4361 (14)	0.2428 (6)	0.3921 (13)
C(5)	0.3533 (11)	0.2771 (7)	0.4766 (11)
C(7)	0.3075 (15)	0.2226 (7)	0.5602 (15)
C(8)	0.2460 (13)	0.3050 (9)	0.4102 (14)
C(6)	0.4054 (12)	0.3399 (6)	0.5364 (11)
C(1)	0.4597 (12)	0.3906 (6)	0.4570 (12)
O(1)	0.4744 (07)	0.4539 (4)	0.4860 (07)
Ligand C			
N(2)	0.4324 (09)	0.5406 (5)	0.3118 (08)
O(2)	0.3825 (07)	0.5120 (5)	0.2339 (07)
C(2)	0.3955 (09)	0.6020 (6)	0.3587 (10)
C(3)	0.2954 (10)	0.6423 (7)	0.3285 (11)
O(3)	0.2374 (08)	0.6247 (5)	0.2473 (09)
C(4)	0.2676 (10)	0.7070 (7)	0.3956 (14)
C(5)	0.3121 (11)	0.7029 (7)	0.5179 (12)
C(7)	0.2545 (12)	0.6448 (7)	0.5900 (10)
C(8)	0.2916 (15)	0.7792 (7)	0.5742 (16)
C(6)	0.4422 (10)	0.6921 (5)	0.5132 (10)
C(1)	0.4686 (10)	0.6246 (6)	0.4490 (10)
O(1)	0.5550 (07)	0.5890 (4)	0.4714 (06)

^a In this table and throughout this paper, estimated standard deviations are given in parentheses.

UV-visible spectra are analogous to those of other ketoximato complexes of cobalt(III)²⁹ and ruthenium(II).²⁹ The UV bands are attributed to a $\pi \rightarrow \pi^*$ transition essentially located in the ligand and are analogous to the $\pi \rightarrow \pi^*$ absorption seen in the free ligand (ϵ 20 000). The visible bands are attributed to charge-transfer transitions.

Crystal Structure of Co(dmho)₃. The final positional parameters for all nonhydrogen atoms of Co(dmho)₃ with the numbering scheme used in Figure 1 are listed in Table I. The unit cell contains four discrete well-separated Co(dmho)₃ molecules, the nearest intermolecular approach being 3.1 Å. Only van der Waals bonds are implicated in intermolecular contacts in the packing of the crystal.

The molecular structure (Figure 1) consists of monomeric tris(5,5-dimethylcyclohexane-1,2,3-trione 2-oximato-*N,O*¹)-cobalt(III). The cobalt(III) center is six-coordinated in a slightly distorted octahedral configuration. Each molecule contains three five-membered chelate rings, each dmho⁻ ligand being bidentate through O(1) and N(2) atoms. The coordinating atoms are disposed on opposite triangular faces in a facial (*fac*) configuration as expected from the known structure of other ketoximato tris chelates.^{7-9,19-21}

Bond lengths and angles of the inner coordination sphere of cobalt are given in Table II. The two triangular faces

Table II. Bond Distances (Å) and Bond Angles (Deg) in the Inner Coordination Sphere of Co in Co(O₃C₈H₁₀N)₃

Distances			
Co-N(2)A	1.87 (1)	Co-O(1)A	1.910 (8)
Co-N(2)B	1.89 (1)	Co-O(1)B	1.923 (8)
Co-N(2)C	1.87 (1)	Co-O(1)C	1.923 (8)
Angles			
O(1)A-Co-N(2)A	84.8 (6)	Co-N(2)A-O(2)A	124 (1)
O(1)B-Co-N(2)B	84.2 (7)	Co-N(2)B-O(2)B	124 (1)
O(1)C-Co-N(2)C	85.2 (6)	Co-N(2)C-O(2)C	125 (1)
Co-N(2)A-C(2)A	113 (1)	Co-O(1)A-C(1)A	112 (1)
Co-N(2)B-C(2)B	112 (1)	Co-O(1)B-C(1)B	112 (1)
Co-N(2)C-C(2)C	113 (1)	Co-O(1)C-C(1)C	111 (1)

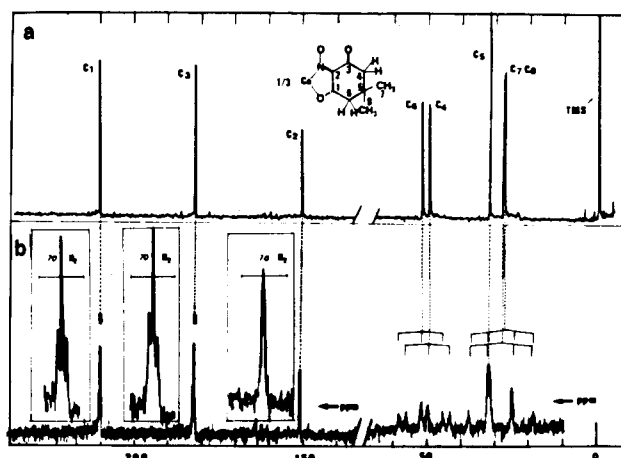


Figure 2. (a) Proton-noise-decoupled ¹³C NMR spectrum of tris(5,5-dimethylcyclohexane-1,2,3-trione 2-oximato)cobalt in CDCl₃. The experimental conditions are selected to optimize the intensities of the quaternary carbon signals. (b) Proton-coupled ¹³C NMR spectrum by the gated-decoupling technique of Co(dmho)₃ in CDCl₃. The expansions of the low-field signals are boxed.

N(2)A, N(2)B, N(2)C and O(1)A, O(1)B, O(1)C are almost parallel to one another. The high charge of the Co(III) causes an increase of the O-Co-N angles and shortening of the Co-O and Co-N bond lengths by comparison with parent ketoximato complexes of iron(II)⁸ and ruthenium(II).^{20,21} The wrapping of the chelate rings about the cobalt is found to be Λ . Indeed, the racemic mixture is spontaneously resolved into one single enantiomer upon crystallization. The three chelate rings A, B, and C, are strictly planar.

There are no significant differences in the interatomic distances and angles of the three ligands A, B, and C. Nevertheless two conformations are found for the three cyclohexane rings in Co(dmho)₃: A, B = λ' and C = δ' . The particular crystal for which the structure was determined contains only the $\Lambda(\lambda'\lambda'\delta')$ isomer (Figure 1).

NMR Spectroscopy. The ¹H NMR spectra of Co(dmho)₃ and H[Ru(dmho)₃] exhibit resonances at the following, respectively: 1.12 (C(7)H₃, C(8)H₃), 2.43 (C(6)H₂), 2.90 (C(4)H₂) ppm; 1.12 (C(7)H₃, C(8)H₃), 2.38 (C(6)H₂), 2.83 ppm (C(4)H₂). The free proton of H[Ru(dmho)₃] is characterized by pH metry in water. The fact that the ¹H NMR spectra display only three signals with the respective intensity ratio 3:1:1 could indicate three equivalent coordinated dmho⁻ ligands in a facial configuration. Indeed the possibility of geometrical changes within the time scale of the NMR measurements may be ruled out.³⁰ The inertness of low-spin Co(III) and Ru(II) complexes is not in favor of a rapid equilibrium *fac* \rightleftharpoons *mer* with bond-rupture motion³¹ at room temperature. The ¹H

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NMR spectra of $\text{Co}(\text{dmho})_3$ and $\text{H}[\text{Ru}(\text{dmho})_3]$ suggest fluxional cyclohexane rings for these complexes. Indeed, with a rigid structure, the two methylene protons H(4) or H(6) are not magnetically equivalent; nevertheless, each methylene group displays one single ^1H NMR signal, in good accordance with fluxional cyclohexane rings. The stereochemistry of the compounds in solution is better clarified with ^{13}C NMR spectroscopy. The proton-decoupled natural-abundance ^{13}C NMR spectra of $\text{Co}(\text{dmho})_3$ (Figure 2a) and $\text{H}[\text{Ru}(\text{dmho})_3]$ contain eight distinct signals. The intensities of the signals corresponding to the quaternary carbons are optimized by selected experimental conditions (see Experimental Section). The fact that the ^{13}C NMR spectra display only eight signals suggests, as for the ^1H NMR data, three equivalent coordinated ligands in solution.

The proton-coupled spectra obtained by the gated-decoupling technique give the unequivocal assignment of the ^{13}C resonances (Figure 2b). Generally the magnitude of ^{13}C - ^1H one-bond coupling constants 1J is found to be around 125 Hz for sp_3 -hybridized carbon.³² One-bond coupling of C(7) to three H(7) atoms and C(8) to three H(8) atoms yields quadruplets centered at 28.08 and 28.38 ppm with relative intensities 1:3:3:1. Each component of the quadruplet ^{13}C - ^1H exists with smaller coupling constant values $^3J(^{13}\text{C}-^1\text{H}) < 12$ Hz.³³ Consequently the two expected quadruplets for C(7) and C(8) resonances appear as a single quadruplet because of the width of each component. Only an evaluation of the bond coupling constant values is extracted: $^1J(\text{C}(7)-\text{H}(7)) \approx ^1J(\text{C}(8)-\text{H}(8)) \approx 130$ Hz. An accidental coincidence is observed between one component of the quadruplet and the broad single peak centered at 31.96 ppm, and this latter peak is assigned to the C(5) resonance. Large one-bond ^{13}C - ^1H couplings are also detected for the C(4) and C(6) resonances. They yield two separated triplets (Figure 2b), which are centered respectively at 49.65 and 51.49 ppm with relative intensities of 1:2:1 ($^1J(\text{C}(4)-\text{H}(4)) \approx ^1J(\text{C}(6)-\text{H}(6)) \approx 130$ Hz).³³

Previous assignments of the ^{13}C resonances of the carbon atoms of the chelating ketoximato function are based on spectral comparison of the ketoximato complexes and several (ketonato)cobalt(III) complexes.^{34,35} The present assignment

is based on $^3J(\text{C}(2)-\text{H}(4))$, $^3J(\text{C}(2)-\text{H}(6))$ and $^2J(\text{C}(3)-\text{H}(4))$, $^2J(\text{C}(1)-\text{H}(6))$ couplings. It has been shown earlier that the magnitude of the vicinal $^3J(^{13}\text{C}-^1\text{H})$ coupling constant depends on the Karplus dihedral angle Φ ³⁶ (3J is very small for $\Phi \approx 90^\circ$). The proton-coupled ^{13}C spectrum of $\text{Co}(\text{dmho})_3$ (Figure 2b) exhibits one singlet at 151.85 ppm and two triplets centered at 183.23 and 210.94 ppm, respectively.

The triplets are analogous and nearly symmetrical. The ^{13}C spectrum appears sufficiently first order to permit the extraction of the coupling constants. The two triplets are assigned to the C(3) and C(1) atoms linked to the carbonyl functions ($^2J(\text{C}(1)-\text{H}(6)) = ^2J(\text{C}(3)-\text{H}(4)) = 6.2$ Hz). The singlet at 151.85 ppm is assigned to the C(2) linked to the oxime function. With a rigid structure of the puckered cyclohexane rings, it is not possible to give a first interpretation of the proton-coupled ^{13}C spectrum. However, fast inversion of the ring is consistent both with the apparent equivalence of the two H(4) and the two H(6) protons given by the ^1H NMR spectrum and with the nearly first order appearance of the proton-coupled ^{13}C NMR spectrum. ^{13}C - ^{15}N couplings³⁷ indicate that coordination occurs via N(2) and O(1) atoms in solution, the C(1) signal being more deshielded than the C(3) signal. The ^{13}C NMR spectrum of $\text{H}[\text{Ru}(\text{dmho})_3]$ is very analogous to that of $\text{Co}(\text{dmho})_3$ with eight resonances observed in $(\text{CD}_3)_2\text{SO}$: 27.10 (C(7) or C(8)), 28.95 (C(7) or C(8)), 31.89 (C(5)), 48.45 (C(4)), 52.86 (C(6)), 155.27 (C(2)), 185.56 (C(3)), 204.46 ppm (C(1)). Attempts to examine the conformational preference of the cyclohexane rings in solution by NMR spectroscopy are difficult because of the weak solubility of $\text{Co}(\text{dmho})_3$ and $\text{H}[\text{Ru}(\text{dmho})_3]$ at low temperature in solvents such as CDCl_3 or CD_2Cl_2 . On the basis of the results obtained, it is reasonable to conclude that inversion between conformers is rapid within the time scale of NMR and that there is no conformational preference. Even on fast inversion of the cyclohexane ring the methyl groups C(7) and C(8) cannot be equivalent and the nonequivalence is not conformational in origin.³⁸

Registry No. $\text{Co}(\text{dmho})_3$, 81987-95-3; $\text{H}[\text{Ru}(\text{dmho})_3]$, 81987-96-4; $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$, 13600-98-1; $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4\text{OH}]$, 13859-66-0.

Supplementary Material Available: Listings of anisotropic thermal parameters of the non-hydrogen atoms, least-squares planes and atomic deviations, bond lengths and angles in the ligands, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Notes

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Novel Peroxo Complexes of Thorium Containing Organic Ligands

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There is considerable interest in peroxo complexes of transition metals as such compounds serve as reagents and catalysts in organic synthesis.¹⁻⁵ We have been interested in

extending our studies to the actinide elements uranium⁶ and thorium. Thorium is of interest as an analogue of titanium. The propoxide of the latter element is an especially useful catalyst in epoxidation reactions with *tert*-butyl hydroperoxide.⁷

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