ized.[10-12] For the complexes $Re(acac)_2Cl_2$,[10] $ReCl_2(acac)(PPh_3)_2$,[11] and $[Ph_4As][Re(acac)_2Cl_2]$,[12] the X-ray structural analyses were carried out on the trans isomers (trans phosphines in the case of $ReCl_2(acac)(PPh_3)_2$). Therefore, the geometry of these complexes more closely approaches that of regular octahedral species, than does that of **1**. The bond angles and bond lengths of the acac ligands in these reported structures are very similar to those of **1**. The Re-P bond lengths in *trans*-$ReCl_2(acac)(PPh_3)_2$ (2.485 (4) and 2.469 (4) Å)[11] are also similar to those of **1**.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Table S1), positional parameters for the phenyl group carbon atoms (Table S2), and the thermal parameters (Table S3) and complete listings of bond distances (Table S4) and bond angles (Table S5) (12 pages); tables of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Application of 2D NMR Techniques to Paramagnetic Systems

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Two-dimensional NMR experiments on paramagnetic systems have been seldomly attempted due to their intrinsic difficulties. Paramagnetic systems are characterized by short nuclear relaxation times due to magnetic coupling of nuclear spins with unpaired electrons. 2D spectroscopy in general requires the application of two or more pulses interleaved by variable and fixed delays to allow the development of the coherences required by each particular experiment. During these times before the acquisition, nuclear relaxation processes cause the overall magnetization to relax back to its equilibrium value. As a consequence, the intensities of the cross peaks are predicted to be much smaller than in slow-relaxing systems.

The most common 2D experiments, COSY and NOESY, suffer from additional drawbacks: the fractional intensities of NOESY cross peaks, even under ideal conditions, are of the order of the steady-state NOE effect, $\eta = \sigma/\rho$, which, especially in small paramagnetic molecules, is always much smaller than unity due to the small σ and large ρ values. COSY cross peaks always show antiphase structure within the multiplet, therefore leading to dramatic cancellation of intensities everytime the J splitting is not resolved; in paramagnetic systems this almost always happens. Despite these difficulties a few COSY and NOESY experiments on paramagnetic molecules with relatively long nuclear T_1 values have been reported.[1-5]

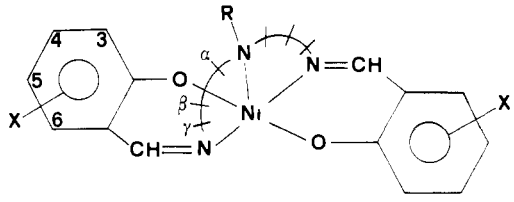
These disadvantages of COSY and NOESY experiments, however, are less severe in other 2D spectroscopies. For instance, chemical exchange effects detected through NOESY type experiments (EXSY) do not have the intrinsic reduced sensitivity of NOE effects. EXSY experiments have been already successfully performed on paramagnetic substances.[3,4,6] Scalar J couplings detected through TOCSY type experiments[7] create cross peaks with in-phase structure of multiplets. This kind of experiment increases the sensitivity for small J values[8,9] and should therefore be more appropriate than COSY experiments in paramagnetic systems.

Experimental Section

The complex [*N*,*N*'-(4-methyl-4-azaheptane-1,7-diyl)bis(5-chlorosalicylideneaminato)]nickel(II) (5-Cl-NiSAL-MeDPT) was prepared as previously reported.[10] The ^1H NMR spectra in $CDCl_3$ were recorded at room temperature on a Bruker MSL300 instrument with a fast low-dynamic range digitizer to cover the entire spectral region. T_1 measurements, in order to minimize the deviation of the pulses from the ideal behavior,[11] were performed with a standard inversion recovery sequence with a composite 180° pulse[12] on four different regions of the spectrum. For HOHAHA experiments the MLEV17 mixing sequence[9] was employed in order to efficiently spin-lock transverse magnetization. EXSY experiments were performed by using the standard phase-sensitive NOESY pulse sequence.

Results and Discussion

We have decided to test the feasibility of HOHAHA and EXSY experiments on the paramagnetic complex 5-Cl-NiSAL-MeDPT. This complex is a member of a family of complexes with general formula reported as follows:



R = CH_3,H

It is known to give rise to well-resolved NMR spectra spread over a very large chemical shift range and to show separate signals for each of the 23 protons except the methyl group. This is due to the fact that the molecule is chiral and lacks a C_2 axis because of the substituent on the apical nitrogen. This also makes the methylene protons of the propylene chains diastereotopic and therefore not equivalent. The assignment of the signals to the various types of protons has been already performed.[13] It was also proposed, but never demonstrated, that interconversion of one enantiomer into the other was possible, although slow on the NMR time scale because it requires breaking of coordination bonds.[14] The choice of the 5-Cl derivative allows us to eliminate the overlap between the H5 proton signals of the ring and the β-CH_2 proton signals of the propylene chains. The spectrum of 5-Cl-NiSAL-MeDPT is shown in Figure 1, together with the assignment. It should be stressed that, due to the large line widths, no J splitting is resolved for any of the ^1H signals.

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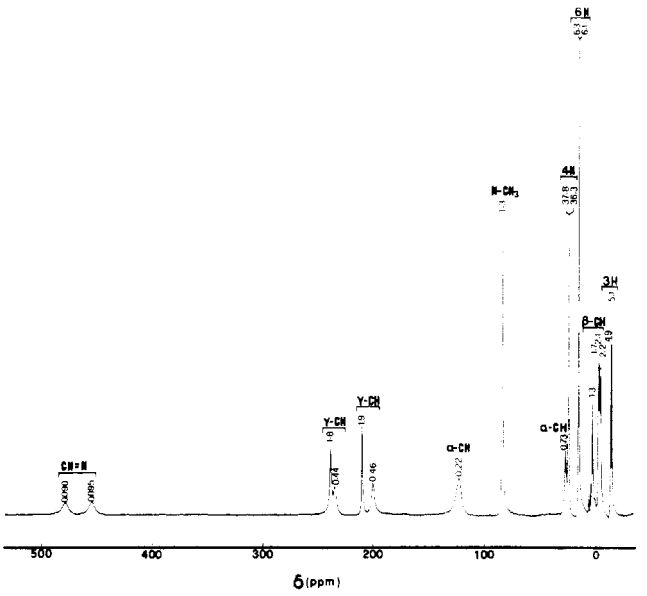

Figure 1. 300-MHz room-temperature ^1H NMR spectrum of a 0.3 M solution of 5-Cl-NiSAL-MeDPT in $CDCl_3$. The T_1 values (ms) of each signal and the assignments are also reported.

In order to plan the 2D experiments and to evaluate the results, the longitudinal relaxation times T_1 of all the signals were measured. The T_1 values are shown in Figure 1. They range from 0.09 ms for the $-CH{=}N$ proton to 37 ms for the H4 protons of the SAL rings. These values are all much shorter than the corresponding values in diamagnetic systems and cover a very large range. Already in the -20 to $+30$ ppm region the proton T_1 values span from 0.7 ms for the α-CH_2 proton to 37 ms for the H4 protons. We have chosen this region to perform the HOHAHA experiment. The 50 ppm range corresponds to a 15.000 Hz bandwidth; the 90° pulse length in the spin-lock field was $\simeq 5$ μs, ensuring that the spin-lock field was more than enough to cover the chosen spectral range. A series of HOHAHA experiments was performed for spin-lock times of 10, 20, and 40 ms. A 2D contour plot for the 20 ms spin-lock time is shown in Figure 2. The presence of strong cross peaks between the H3 and the H4 protons is immediately apparent, showing that HOHAHA experiments can be performed even on fast relaxing signals with unresolved J splitting. Besides these cross peaks arising from scalar couplings, other cross peaks are apparent in the HOHAHA spectrum, for instance between the two H4 protons (inset) and between the two H3 protons. Indeed, there are also four H3-H4 cross peaks instead of two (inset). These cross peaks can only originate from chemical exchange. It is known that chemical exchange and scalar interactions are observed together in rotating-frame experiments.[15] The presence of exchange peaks definitely confirms the earlier predictions about the fluxionality of these systems.[14]

By an increase of the spin-lock time to 40 ms, the H3-H4 cross peaks decrease in intensity, whereas a cross peak between H4 and H6 starts to appear (Figure 3A). By a decrease of the spin-lock time to 10 ms, the ring proton cross peaks almost disappear, while cross peaks start to be apparent between two signals in the region of the β-CH protons (Figure 3B). The latter have T_1 values of $\simeq 2$ ms and therefore suffer more from the choice of relatively long spin-lock times.

Of course, the success of the present experiment depends on the high concentration of the sample that allows detection of cross peaks down to 0.2% relative to the diagonal peaks, which, in turn, have also suffered from loss of intensity due to fast relaxation. On the other hand, a COSY experiment performed over the same time on the same sample gave no evidence of cross peaks above the 0.02% noise threshold (not shown). This confirms the expectation that HOHAHA is the technique of choice for detecting scalar couplings in fast-relaxing systems.

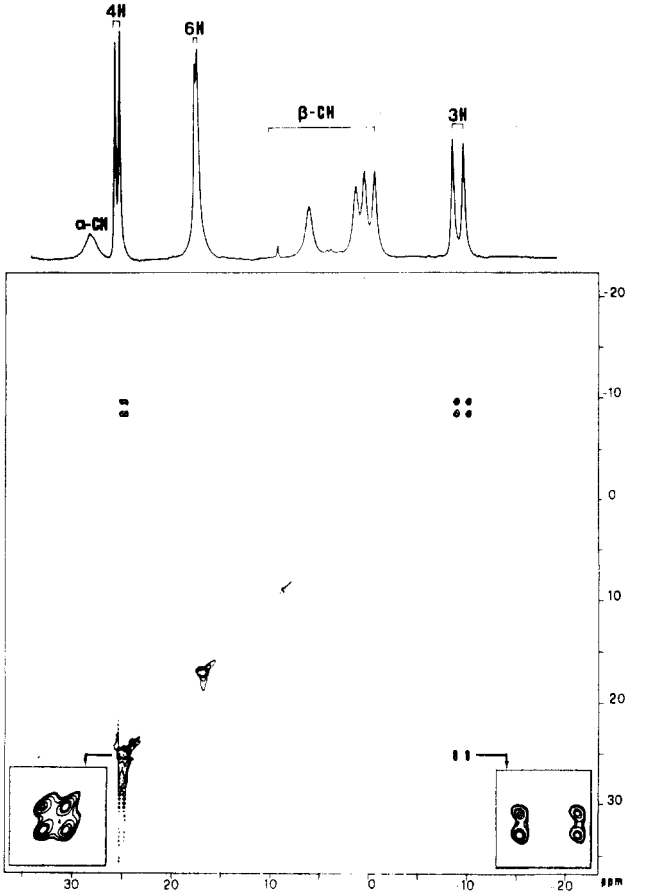

Figure 2. HOHAHA spectrum of 5-Cl-NiSAL-MeDPT in the -20 to $+30$ ppm region recorded with 20-ms spin-lock time. Conditions are as in Figure 1. The inset on the left shows an enlargement of the area around the H4 diagonal peaks, and the inset on the right shows an enlargement of the area around the H3–H4 cross peaks, both with the same contour levels. The diagonal peaks of the β-CH_2 protons are below the contour threshold under the present conditions.

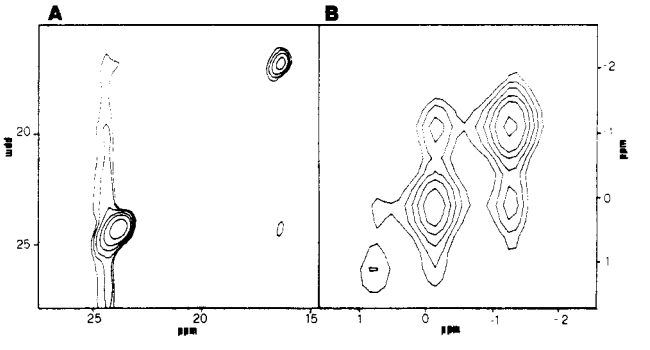

Figure 3. (A) Enlargement of the H4-H6 cross-peak area in the HOHAHA spectrum obtained with 40-ms spin-lock time. (B) Enlargement of the area around a β-CH pair in the HOHAHA spectrum obtained with 10-ms spin-lock time. Conditions are as in Figure 1.

Having established the occurrence of chemical exchange, we have performed also EXSY experiments, with mixing times of 5 and 20 ms. Analogously with the HOHAHA experiments, exchange peaks between ring protons are detected better at 20 ms and between β-CH protons at 5 ms. The latter turn out to be the same pair of protons giving rise to HOHAHA cross peaks (Figure 3B). Therefore, such peaks must arise from corresponding protons in two different chains and not from the geminal protons pair in one of the two chains.

Obviously, no NOESY peaks are observed. Indeed, in such a fast-rotating system the σ values are much smaller than the paramagnetically dominated ρ values, and therefore, NOE effects

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are extremely small. The situation might be different for viscous solutions and/or for macromolecular systems.

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Doubly Bridged μ-Fluoro–μ-Oxo and μ-Fluoro–μ-Hydroxo Chromium(III) Dimers

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Introduction

Dihydroxo-bridged chromium(III) dimers with aromatic amine ligands are susceptible to nucleophilic attack by halide and pseudohalide ions, resulting in the displacement of a single μ-OH^- group.[1,2] Thus, linear oxo-bridged dimers of the type $[L(tmpa)CrOCr(tmpa)L]^{2+}$ (tmpa = tris(2-pyridylmethyl)amine; L^- = NCS^-, NCO^-, CN^-, N_3^-, Cl^-) are formed from the reactions of L^- with $[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+}$ (eq 1).[2] This reaction

$$[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + 2L^- \rightarrow [L(tmpa)CrOCr(tmpa)L]^{2+} + H_2O \quad (1)$$

is not completely general, however, in that Br^-, I^-, and neutral nucleophiles fail to react with the chromium diol (i.e. *N*,*N*-dimethylformamide, urea) or only deprotonate a bridging hydroxo substituent (i.e. ammonia, pyridine). In the course of these studies, it was found that F^- reacts with $[Cr(tmpa)(OH)]_2^{4+}$ to give products other than the anticipated $[Cr(tmpa)F]_2O^{2+}$ cation.[2] We report here the synthesis of $[(tmpa)Cr(O)(F)Cr(tmpa)](ClO_4)_3\cdot H_2O$ and $[(tmpa)Cr(OH)(F)Cr(tmpa)](ClO_4)_4$, the first well-characterized examples of μ-fluoro–μ-oxo and μ-fluoro–μ-hydroxo doubly-bridged chromium(III) dimers.

Experimental Section

The preparations of $[Cr(tmpa)(OH)]_2(ClO_4)_4\cdot 4H_2O$ and $[(tmpa)Cr(O)(OH)Cr(tmpa)](ClO_4)_3\cdot H_2O$ have already been described.[3] Reagent grade chemicals were used throughout. Microanalyses were performed by Desert Analytics (C,H,N; Tucson, AZ) and Galbraith Laboratories (F; Knoxville, TN). Chromium was assayed by the basic peroxide method.[4] Cation-exchange chromatography was carried out at 5 °C on SP-Sephadex C-25-120 resin (Na^+ form), and eluting solutions were prepared from doubly distilled water. Ultraviolet–visible and infrared measurements were acquired on Shimadzu UV-260 and Perkin-Elmer 1600 spectrophotometers, respectively. Cyclic voltammograms of 0.5 mM electroactive solute solutions were acquired with a Bioanalytical Systems CV-1B triangular wave generator and a Hewlett-Packard 7004 B X-Y recorder.[1,5] Working electrodes were referenced to an aqueous saturated calomel electrode in 0.1 M $NaNO_3$; a Pt wire was the auxiliary electrode in all experiments. Reported potentials were converted to the SHE scale as before[5] by using (hydroxyethyl)ferrocene as an internal calibrant. Half-wave potentials were calculated as the mean of anodic and cathodic peak potentials when the $E_{1/2}$ value exhibited no sweep rate dependence from 50 to 300 mV/s.

$[(tmpa)Cr(O)(F)Cr(tmpa)](ClO_4)_3\cdot H_2O$ was prepared by refluxing 2.00 g (1.68 mmol) of $[Cr(tmpa)(OH)]_2(ClO_4)_4\cdot 4H_2O$ with NaF (0.7065 g, 16.8 mmol) in CH_3CN (200 mL) for 1 h. The deep green reaction mixture was then evaporated to 100 mL following the removal of excess NaF from the hot solution by filtration. This filtrate was combined with 400 mL of water to which 1 mL of 4.0 M NaOH had been added to ensure that all of the complex would be present in the μ-oxo–μ-fluoro form. Precipitation of the product was induced by the addition of solid $LiClO_4$, after which digestion of the stirred solid was allowed to proceed for 1 h at 5 °C. The dark brown microcrystalline product was collected by filtration, washed with triply distilled water, and air-dried (1.05 g, 60%). Anal. Calcd for $Cr_2C_{36}H_{38}N_8Cl_3FO_{14}$: Cr, 10.04; C, 41.73; H, 3.70; N, 10.81; F, 1.83. Found: Cr, 9.98; C, 42.01; H, 3.82; N, 10.88; F, 1.48. UV–vis (CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 256 (21 500), 298 (4650), 330 (4620), 386 (2940), 418 (2520). IR (KBr pellet; cm^{-1}): 3422 vs, 1609 s, 1484 w, 1438 m, 1400 w, 1290 w, 1158 m, 1090 vs, 1031 m, 906 w, 881 m, 766 s, 736 w, 723 w, 669 m, 655 m, 623 s.

$[(tmpa)Cr(OH)(F)Cr(tmpa)](ClO_4)_4$ was prepared as above, except that a crude product from evaporation of the reaction mixture in CH_3CN was recrystallized quickly by addition of $LiClO_4$ to a *neutral* aqueous solution. The red-brown solid was filtered off and air-dried. Anal. Calcd for $Cr_2C_{36}H_{37}N_8Cl_4FO_{17}$: Cr, 9.30; C, 38.66; H, 3.33; N, 10.02. Found: Cr, 9.28; C, 38.66; H, 3.60; N, 9.79. UV–vis (H_2O, 0.01 M HBr; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 261 (15 800), 387 (222), 537 (281).

Results and Discussion

Fluoride ion combines readily with the tmpa chromium(III) diol in refluxing acetonitrile according to eq 2, leaving no trace of either unreacted starting material or the expected product,

$$[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + F^- \rightarrow [(tmpa)Cr(O)(F)Cr(tmpa)]^{3+} + H_2O \quad (2)$$

$[Cr(tmpa)F]_2O^{2+}$. The corresponding μ-fluoro–μ-hydroxo complex is easily isolated following the protonation of $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ by water. An attempt to grow large crystals of $[(tmpa)Cr(OH)(F)Cr(tmpa)](ClO_4)_4$ by digestion in 0.02 M $HClO_4$ for 6 h at 5 °C resulted in the recovery of a decomposition product, $[Cr(tmpa)(OH)]_2(ClO_4)_4\cdot 4H_2O$, identified from its spectroscopic and acid–base properties.[3] In a similar fashion, $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ is highly susceptible to base-induced hydrolysis even in weakly alkaline solutions. Although detailed kinetic studies have not been performed, repetitive spectra of aqueous $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ show that the intense, near-ultraviolet bands decay over a period of 2 h at ambient temperature. In contrast, $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ strongly resists base hydrolysis in the pH 8–11 interval.[3] This sensitivity to water and the tendency of both complexes to precipitate as fine powders from non-aqueous solvents has prevented us from obtaining crystals of sufficient quality for X-ray crystallographic structural analysis.

The identities of both complexes may be inferred from elemental analyses, electronic and infrared spectra, and reactivity studies of aqueous solutions. Thus, the possibility that the complex with empirical formula $Cr_2C_{36}H_{38}N_8Cl_3FO_{14}$ contains $[(H_2O)(tmpa)CrOCr(tmpa)(F)]^{3+}$ or $[(OH)(tmpa)Cr(OH)Cr(tmpa)(F)]^{3+}$ rather than $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ cations is ruled out by the failure of this material to exhibit neutralization of the putative H_2O or μ-OH^- ligands in strongly alkaline media, affording a diperchlorate salt. Furthermore, the rapid and reversible protonation of this complex to $[(tmpa)Cr(OH)(F)Cr(tmpa)]^{4+}$, monitored spectrophotometrically in aqueous solution, is most easily understood in terms of a bridging hydroxide ligand with pK_a near 7, analogous to those of $[Cr(tmpa)(OH)]_2^{4+}$ (pK_{a1} = 7.50, pK_{a2} = 12.4; 25 °C, I = 0.1 M).[3] The facile conversion of the complex with empirical formula $Cr_2C_{36}H_{37}N_8Cl_4FO_{17}$ to $[(Cr(tmpa)(OH)]_2(ClO_4)_4\cdot 4H_2O$ in acidic solution implicates a dinuclear precursor, and absorption peaks at 387 and 537 nm correspond closely in both position and intensity to the d–d bands of $[Cr(tmpa)(OH)]_2^{4+}$ at 385 (ϵ = 226 M^{-1} cm^{-1}) and 540 nm (ϵ = 262).[3] The electronic spectrum of $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ is not well-resolved, showing only a single near-ultraviolet peak at 370 nm (ϵ = 900 M^{-1} cm^{-1}) superimposed on a rapidly rising absorption envelope.[3] A striking similarity may be noted, however, between the spectra of $[(tmpa)Cr(O)(F)Cr(tmpa)]^{3+}$ and $[(tmpa)Cr(O)(CH_3CO_2)Cr(tmpa)]^{3+}$, for which

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