# Coordination Chemistry of Glyphosate: Structural and Spectroscopic Characterization of Bis(glyphosate)metal(III) Complexes

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Glyphosate (*N*-(phosphonomethyl)glycine, PMG) is a widely used, commercially available herbicide which is degraded and immobilized upon contact with soil. Since metal ions are believed to play a role in this process, the coordination chemistry of glyphosate is of significant interest. Although several 1:1 metal complexes of glyphosate have been structurally characterized, no 2:1 complexes have been characterized other than by potentiometric titration. The present work describes the synthesis and crystal structure of $Na_3Co(PMG)_2{\cdot}11H_2O$ as well as a spectroscopic study of the chromium complex. There are potentially eight geometric isomers for such a $ML_2$ complex, all of which are formed in solution in the reaction of $Na_3Co(CO_3)_3$ or $CoCl_2/H_2O_2$ with PMG. The individual isomers are not separable due to rapid interconversion, despite the expected kinetic inertness of $Co^{3+}$, and have been characterized by various 1D and 2D NMR methods as well as UV spectroscopy. The structurally characterized *fac-RS-all-trans* isomer produces all the other isomers upon dissolution in water. On the basis of kinetic data, a twist as well as an associative interchange mechanism is proposed for these isomerization processes. The most symmetric *fac-RS-all-trans* isomer crystallized as the trisodium salt from an equilibrium mixture of all isomers in $H_2O$/ethanol and was characterized by single-crystal X-ray diffraction. The compound $Na_3Co(PMG)_2{\cdot}11H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.131(2)$ Å, $b = 11.316(3)$ Å, $c = 11.911(4)$ Å, $V = 1190.4\ (5)$ Å$^3$, $\alpha = 97.21(3)°$, $\beta = 109.47(3)°$, $\gamma = 107.29(3)°$, and $Z = 2$; the two metal complexes in the asymmetric unit are essentially identical. The symmetry of each complex anion is $C_i$, implying opposite configurations at the nitrogens of the glyphosate ligands and an achiral molecule. The structure was determined from 3099 unique data measured at −96 °C. Refinement of 319 variables against 1615 observed data gave $R = 5.2\%$, $R_w = 5.5\%$, and GOF = 1.506.

## Introduction

The compound *N*-(phosphonomethyl)glycine, or glyphosate, is the active ingredient in the commercially available herbicide Roundup. Since its discovery as a herbicide at Monsanto in the early 1970s,[1] it has been the subject of numerous biological and chemical studies. Because of its unique properties[2] it has been described as the ideal herbicide; sales reached one billion dollars in 1986. One of its most remarkable properties is that glyphosate is immobilized and degraded in the soil within a few days to the nontoxic products $CO_2$, $PO_4^{3-}$, and $NH_3$ (expensive fertilizer). In this process metal complexation must play a role.

Various aspects of the coordination behavior of glyphosate have been examined by several research groups. Madsen et al.[3] determined the stability constants of the divalent complexes $ML^-$ (M = Cu, Zn, Mn, Ca, Mg; L = glyphosate trianion) by potentiometric titration. More extensive investigations by Motekaitis and Martell[4] established the tendency of divalent alkaline-earth and transition metals, as well as some trivalent metal ions, to form 1:1 and 2:1 metal chelates with glyphosate in solution. Crystal structures have been reported only for the 1:1 Ca(II)[5,6] and 1:1 Cu(II)[7] complexes of glyphosate. Both have been shown to be polymeric. While glyphosate is not coordinated through its protonated nitrogen in the Ca(II) complex, it does act as a tridentate ligand in the Cu(II) complex.

NMR studies of platinum glyphosate complexes[8] showed that glyphosate may be bound as a tridentate ligand in these square planar complexes within certain pH ranges. In 2:1 complexes of octahedral metal ions, glyphosate is expected to be a tridentate ligand. Although crystal structures of several 2:1 metal complexes of the related compound iminodiacetic acid (IDA) are known for both the *cis*[9] and *trans*[10,11] facial isomers, no crystal structure of any 2:1 PMG metal complexes have been reported.

Once the nitrogen of glyphosate is attached to a metal atom, its stereochemistry is fixed, adopting either an *R* or *S* configuration. All the possible isomers of a $M(PMG)_2^{3-}$ complex, where M is any tricationic metal ion and PMG acts as a tridentate ligand, are depicted schematically in Figure 1. These isomers can be distinguished in part by their symmetry. Only the facial *RS-all-trans* isomer is achiral due to its $C_i$ symmetry. All the other isomers depicted in Figure 1 are either asymmetric or dissymmetric ($C_2$ symmetry) and are therefore chiral.

We report here the synthesis of $Na_3Co(PMG)_2$, its solution chemistry, and the crystal structure of the most symmetric *fac-RS-all-trans* isomer.

## Experimental Section

**Physical Measurements.** UV–vis spectra were recorded with the use of a 1-cm path length cell on a HP8450A spectrophotometer. All NMR spectra were recorded in $D_2O$ at the College of Chemistry facility, University of California at Berkeley. $^1$H-NMR, long range $^1$H–$^1$H correlated 2D-COSY, the 2D-NOESY, and the $^1$H–$^{13}$C (hetero COSY) spectra were recorded on a Bruker AM 500 instrument. $^{13}$C and $^{31}$P NMR spectra and the $^{31}$P–$^1$H correlated spectrum (hetero COSY) were

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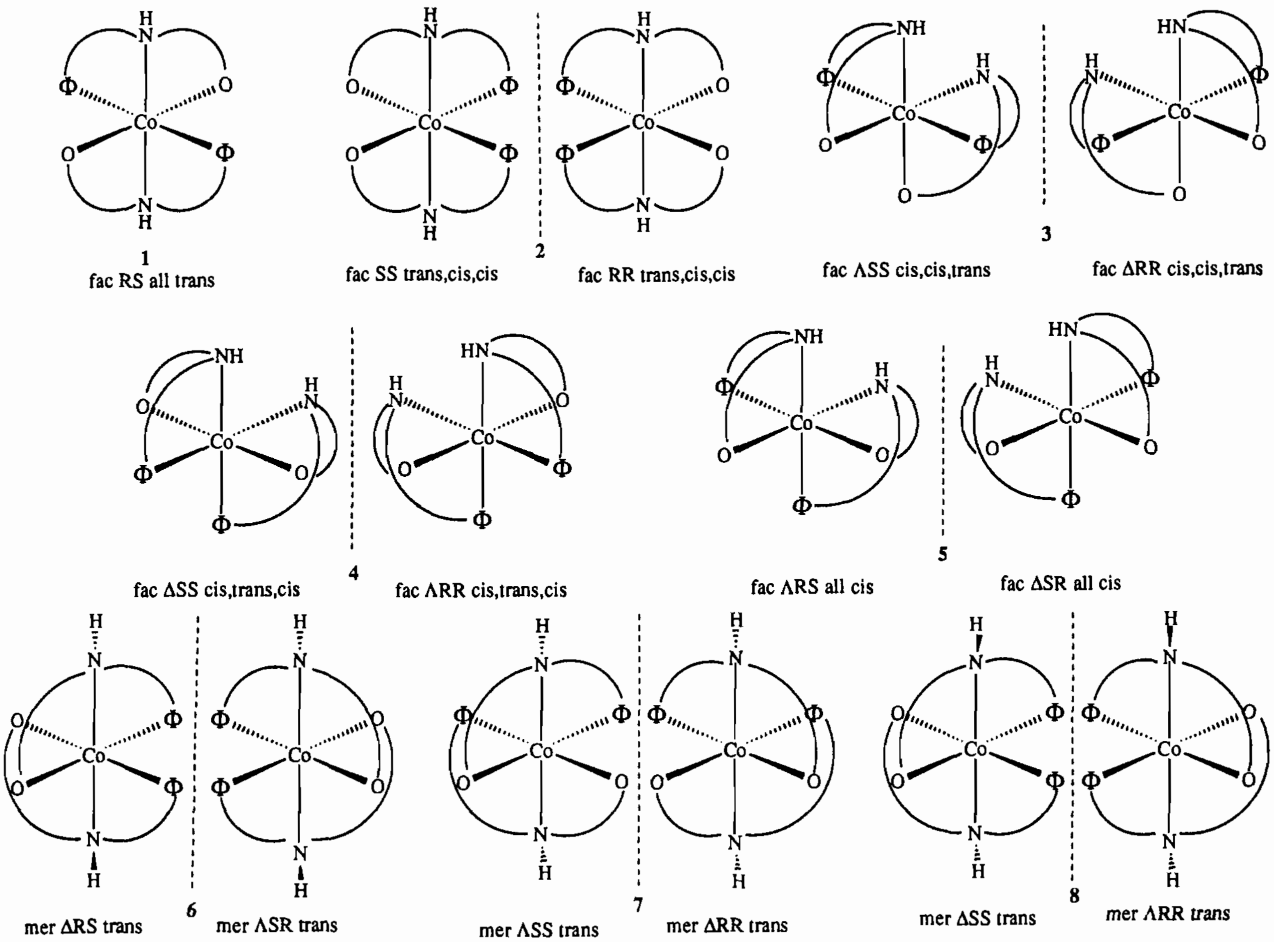

fac RS all trans

fac SS trans,cis,cis

fac RR trans,cis,cis

fac ΛSS cis,cis,trans

fac ΔRR cis,cis,trans

fac ΔSS cis,trans,cis

fac ΛRR cis,trans,cis

fac ΛRS all cis

fac ΔSR all cis

mer ΔRS trans

mer ΛSR trans

mer ΛSS trans

mer ΔRR trans

mer ΔSS trans

mer ΛRR trans

**Figure 1.** Schematic depiction of the possible $[Co(PMG)_2]^{3-}$ isomers. Key: $\Phi = CH_2PO_3^{2-}$; O = $CH_2CO_2^-$.

recorded on a Bruker AMX 400 instrument. Microanalytical and atomic absorption analyses were performed by the analytical laboratory at the University of California at Berkeley.

**Syntheses and Materials.** Glyphosate was obtained as the pure crystalline acid (99.9%) as a gift from Monsanto. The salt $Na_3Co(CO_3)_3$ was prepared according to the literature procedure.[12] All other materials were reagent grade and used as received.

**$[Co(PMG)_2]^{3-}$ Syntheses. Preparation of $Na_3Co(PMG)_2$ via $Na_3(CO_3)_3$.** Glyphosate (1.699 g, 10 mmol) was dissolved in 30 mL of $H_2O$ (1.810 g, 5 mmol). $Na_3Co(CO_3)_3$ was added in small portions. The resulting red brown solution was stirred for 2 h, and the solvent was removed under vacuum. The brown residue was redissolved in 2 mL of $H_2O$. This solution was chromatographed on Chelex (pH = 10.7–10.8) to remove cobaltous impurities. The Co(III) complex eluted as a large band that had a brownish color at its head and a blue color at its tail. It was not possible, however, to separate a brown band from a blue band by chromatography. If the reaction mixture was stirred overnight, the large band was predominantly blue. The band was collected and the solvent removed under vacuum. A red brown solid containing a mixture of different $Na_3Co(PMG)_2$ isomers was obtained. The solid was dried in a vacuum oven at 40 °C. Anal. Calcd (found) for $C_6H_{10}CoN_2Na_3O_{10}P_2$: C, 15.66 (14.54); H, 2.19 (2.55); N, 6.09 (5.10), Co 12.81 (13.8). The NMR spectra showed a mixture of different isomers, which are discussed herein.

**Preparation of $Na_3Co(PMG)_2$ via $CoCl_2$.** Glyphosate (1.699 g, 10 mmol) was dissolved in 30 mL of $H_2O$, and the pH was adjusted to 8–8.5 with NaOH (1M). Upon addition of $CoCl_2 \cdot 6H_2O$ (1.190 g, 5 mmol) the pH dropped to ~6. The pH was raised again to ~8 with NaOH (1 M), and the resulting solution was treated with 0.1 mL of 30% $H_2O_2$ to oxidize Co (II) to Co (III). The color of the solution changed from slight pink to dark wine red. After stirring the solution overnight the color changed to dark blue. The Co complex was purified as described above.

**Preparation of $(NH_4)_3Co(PMG)_2$.** Glyphosate (1.699 g, 10 mmol) was dissolved in 30 mL of $H_2O$, and the pH was raised with an $NH_3$ (1 M) solution to ~8. After addition of $CoCl_2$ (1.190 g, 5 mmol) the pH was raised again with 4 M $NH_3$ to ~8. The resulting solution was treated with 0.1 mL of 30% $H_2O_2$ to oxidize the Co(II) to Co(III). The reaction mixture was stirred overnight. The purification of the Co complexes was the same as described above. The solid obtained from this reaction was highly deliquescent and could not be characterized by micronalysis. The $^1$H-NMR spectrum showed the same mixture of isomers as did the trisodium salt.

**Preparation of $(^iPr_4N)_3Co(PMG)_2$.** The similar compound $(^iPr_4N)_3Co(PMG)_2$ was synthesized using the procedure described for the $(NH_4)_3Co(PMG)_2$ complex, except the pH was adjusted with a 10% $(^iprop_4N)^+OH^-$ solution. As above, the solid obtained was highly deliquescent and could not be characterized by microanalysis. The $^1$H-NMR spectrum showed the same mixture of isomers as did the trisodium salt.

**Preparation of $Na_3Cr(PMG)_2$.** Glyphosate (0.676 g, 4 mmol) was dissolved in 10 mL of $H_2O$. The pH was raised to ~6.2 with 1 M NaOH. To this solution, $CrCl_3 \cdot 3H_2O$ (0.425 g, 2 mmol) dissolved in 10 mL of $H_2O$ was added, dropping the pH to ~3. The pH was raised again to 6 and the resulting blue solution was heated for 30 min. The solvent was then removed under vacuum.

The blue residue was dissolved in a MeOH/$H_2O$ (1:1) solution and applied to a Sephadex LH-20 column (2.7 × 30 cm) and eluted with MeOH/$H_2O$ (1:1). Unreacted $CrCl_3$ was eluted first as a green band, followed by a blue band containing the $Na_3Cr(PMG)_2$ complex. The blue band was collected, the solvent removed under vacuum, and the blue residue dried in a vacuum oven at 40 °C. The microanalysis showed that the $Na_3Cr(PMG)_2$ complex was not obtained in a pure state. Although the parent ion peak (M: $z/e = 453$) of the $Na_3Cr(PMG)_2$ complex was present in the FAB spectrum, the strongest peak was found to be at 475.9 (M + Na), and the highest mass at 768.8. The UV spectrum of the blue solid in $H_2O$ showed two strong absorption bands at 412 and 562 nm, respectively (see Figure 2).

**Crystallization of $Na_3Co(PMG)_2$ (Isomer 1).** The red brown $Na_3Co(PMG)_2$ complex (300 mg) was dissolved in 2 mL of $H_2O$, and ethanol was added dropwise until the formation of a cloudy precipitate which would not redissolve upon stirring. A drop of $H_2O$ was then added and the solution kept at ~5 °C for several days. Very small needlelike purple

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[12] Collman, J. P.; Kittleman, E. T. *Inorg. Synth.* **1966**, *8*, 149–153.

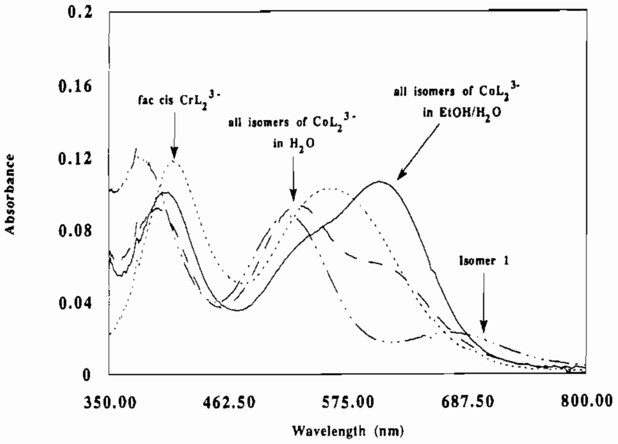

**Figure 2.** UV spectra: all isomers in water (wide dashed line); all isomers in EtOH/water (solid line); isomer 1 (intermittent dashed line); chromium complex $CrL_2^{3-}$ (narrow dashed line).

**Table 1.** Absorption Maxima of the Glyphosate Complexes

| isomer | abs (max), nm |
|---|---|
| isomer **1** | 381, 518, 662 nm |
| mixture of isomers in $H_2O$ | 397, 528, 620 (sh) |
| mixture of isomers in $H_2O$/EtOH | 400, 536 (sh), 604 |
| chromium complex | 412, 562 |

crystals were obtained from this solution. Both $^1H$- and $^{31}P$-NMR spectra of these crystals taken immediately after dissolution showed only the peaks of **1**. The microanalysis of the purple crystals indicated the presence of 11 waters of crystallization, which was confirmed by the crystal structure. Anal. Calcd (found) for $C_6H_{10}CoN_2Na_3O_{10}P_2 \cdot 11\ H_2O$: C, 10.95 (11.05); H, 4.90 (4.67); Co 8.95 (10.70); N, 4.26 (4.13); Na, 10.48 (9.27); P, 9.41 (9.60).

The same procedure was used to obtain highly deliquescent crystals from the $(NH_4)_3Co(PMG)_2$ complex. The $^1H$-NMR spectrum showed the same mix of isomers as did the sodium salt of the complex. No crystals could be obtained from the $(^i prop_4N)_3Co(PMG)_2$ complex.

**Crystallization from Deuterated Solvents.** Pure isomer **1** (100 mg) was dissolved in 0.5 mL of $D_2O$ and the solution was allowed to stand overnight. The $^1H$-NMR spectrum was recorded, showing that the solution had the composition of the equilibrium mixture (*vide infra*). To this solution, acetone-$d_6$ was added dropwise until the cloudy precipitate would not redissolve upon stirring; one drop of $D_2O$ was added, and the precipitate redissolved immediately. This solution was kept at 4 °C for several days. The blue mother liquor was separated with a Pasteur pipet from the purple crystals (isomer **1**) that formed out of this solution. The $^1H$ NMR of the blue mother liquor taken at 4 °C showed that isomer **3** was the major component in this solution. When the solution was warmed to room temperature, the ratio of **1**:**3** remained the same. The ratio **1**:**3** increased in favor of **1** only if the $^1H$-NMR spectrum was recorded at 60 °C.

**Time-Dependent $^1H$-NMR Spectra of Isomer 1.** Pure **1** (13.5 mg) was dissolved in 0.5 mL of $D_2O$ with trace amounts of DMSO as in inert integration standard. A $^1H$-NMR spectrum (500 MHz) was recorded every 2 min (8 scans per spectrum) and the disappearence of **1** and the formation of the other isomers was followed by integrating characteristic peaks of each isomer. All measurements were done at room temperature (21 ± 1 °C).

**UV Spectra.** UV spectra of solutions of freshly dissolved isomer **1** in $H_2O$, of equilibrium mixtures of the different isomers in $H_2O$, and of an equilibrium mixture in $EtOH/H_2O$ (containing mainly **3**) were recorded. (The UV spectrum of the chromium complex was taken in $H_2O$.) The absorption maxima are listed in Table 1, and the spectra are shown in Figure 2.

## X-ray Crystallography

A small, dark purple needlelike crystal of the sodium salt of **1** (which was fractured approximatedly along its long axis) was isolated from a batch of very tiny and thin crystals. A small fragment (0.35 × 0.10 × 0.05 mm) was cut and mounted in Paratone on a glass capillary at −96 °C. Peaks from two crystallites were separated by up to 1° in some areas, easily resolved into two sharp peaks (average peak width = 1.1° at $\theta = 12°$). Two slightly offset sets of the same six reflections and their Friedel pairs were independently collected and separate orientation matrices for the two crystallites used for manual centering and indexing. The crystal system was found to be triclinic with cell parameters given in Table 2. The average orientation matrix from these 12 reflections from both crystallites was used during data collection in order to center collection between split peaks. No orientation checks were done during data collection. Data were collected as $\omega$ scans with a 2.00° 2Θ base width using the NEEDLE subroutine[13] oriented along the plane of the fracture (032), as evidenced by superimposed peaks of the two crystallites. This insured collection of both crystallite peaks within the scan width throughout reciprocal space. A total of 3119 data were collected, of which 1615 had $F^2 > 3\sigma(F^2)$. No correction for crystal decomposition was necessary, and no absorption correction was applied (min(av) absorption from azmithal scan data = 0.93).

**Table 2.** Summary of Crystal Data for Compound **1**

| | |
|---|---|
| formula | $C_6H_{34}CoN_2Na_3P_2O_{21}$ |
| fw | 658.17 |
| temp, °C | −96 |
| crystal syst | triclinic |
| space group | $P\bar{1}$ (No. 2) |
| Cell Consts[a] | |
| *a*, Å | 10.131(2) |
| *b*, Å | 11.316(3) |
| *c*, Å | 11.911(4) |
| $\alpha$, deg | 97.21(3) |
| $\beta$, deg | 109.47(3) |
| $\gamma$, deg | 107.29(3) |
| *Z* | 2 |
| *V*, Å$^3$ | 1190.4(5) |
| abs coeff ($\mu_{calc}$), cm$^{-1}$ | 9.95 |
| $\delta_{calc}$, g/mL | 1.836 |
| F(000) | 680 |
| cryst dimens, mm | 0.35 × 0.10 × 0.05 mm |
| radiation | Mo-K$\alpha$ ($\lambda$ = 0.71073 Å) |
| diffractometer | Enraf-Nonius CAD-4 |
| *h*, *k*, *l* range collcd | $0 \rightarrow 10, -12 \rightarrow 11, -12 \rightarrow 11$ |
| 2$\theta$ range, deg | 3.0–45.0 |
| scan type | $\omega$, 2.00° base width |
| scan speed ($\theta$), deg/min | 8.24 |
| no. of reflcns collcd | 3119 |
| no. of unique reflcns | 3099 |
| no. of reflcns with ($F_o^2 > 3\sigma(F_o^2)$) | 1615 |
| no. of params | 319 |
| data/param ratio | 5.1 |
| $R = [\Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert]$ | 0.052 |
| $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]$ | 0.055 |
| GOF | 1.506 |
| final diff $\rho_{max}^+/\rho_{max}^-$, e$^-$/Å$^3$ | +0.526[b]/−0.245[c] |

[a] Unit cell parameters and their esd's were derived by a least-squares fitting of the average setting angles of the same 12 reflections from each of two crystallites in the range 23.82° ≤ 2$\theta$ ≤ 24.86°. [b] Located near Co2. [c] Located near Na1.

The space group was found to be $P\bar{1}$, with two crystallographically independent complexes in the unit cell (Z = 2). The structure was solved from a Patterson map (Co, P, Na positions). Both Co1(0,0,0) and Co2-(0.5,0,0) sit on special positions with inversion symmetry. The complexes are approximately related by a 2-fold screw axis along *a*. All atoms were refined anisotropically, except hydrogens, whose positions were predicted and included in the structure factor calculation, but not refined. The final residuals for 319 variables were *R* = 5.19%, $R_w$ = 5.50%, and GOF = 1.506.

## Results and Discussion

**Synthesis, Purification, and Characterization of the Cobalt Isomers.** Glyphosate reacts with $Na_3Co(CO_3)_3 \cdot 3H_2O$ in water at room temperature to give a mixture of different isomers of $Na_3Co(PMG)_2$. The same mixture was obtained by the combination of $CoCl_2$ with glyphosate and subsequent oxidation with $H_2O_2$. Both methods represent classical approaches to the synthesis of $Co^{III}L_2$ complexes, where L is any tridentate ligand. The second method requires control of the pH, but allows free

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[13] NEEDLE collection subroutine, Enraf-Nonius Delft CAD4, Version 5.0, 1989.

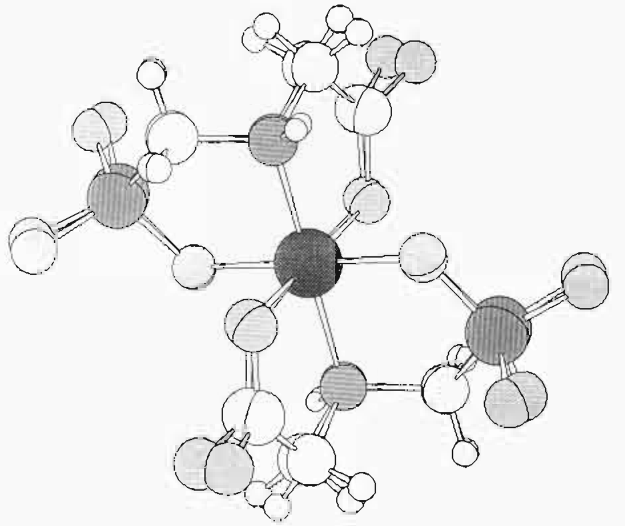

**Figure 3.** Minimized superposition of the two crystallographically independent $Co(PMG)_2^{3-}$ molecules in the unit cell. RMS deviations are given in Table S5 (supplementary material).

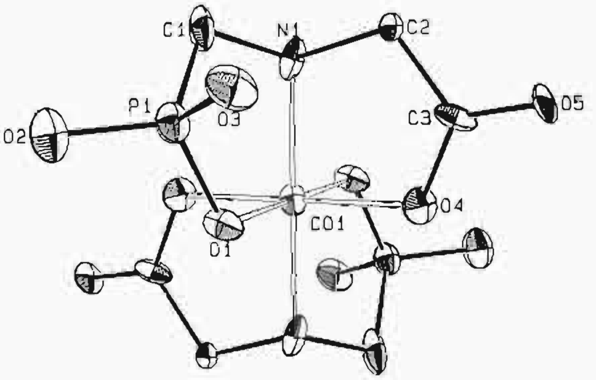

**Figure 4.** ORTEP plot of one $[Co(PMG)_2]^{3-}$ molecule (Co1 at 0, 0, 0).

choice of the cationic counterion. Cobaltous impurities could be removed by Chelex chromatography. Proton NMR spectra of the diamagnetic cobalt complexes indicated the presence of several different isomers. Although Co(III) complexes should be kinetically inert due to their $d^6$ configuration, it was not possible to separate the isomers by HPLC. Microanalysis of the isomeric mixture gave a glyphosate:cobalt ratio of 2:1. Addition of a less polar solvent such as ethanol or acetone to the isomeric mixture in $H_2O$ led to the crystallization of pure isomer **1**. If **1** was dissolved in $H_2O$, a purple solution was formed, whose color changed within a few minutes to blue, and became a very dark blue solution after 2 h. The resultant solution is a mixture of all isomers.

**Discussion of the Crystal Structure.** The crystal structure of $Na_3[Co(PMG)_2]\cdot 11H_2O$ consists of two crystallographically independent molecules in the asymmetric unit. Both molecules are essentially identical and are therefore discussed together, with the values for the second given in square brackets behind the values for the first. The superposition of the two structures (Figure 3) emphasizes the similarity of the coordination geometry about the two independent cobalt ions. The RMS deviation of minimized differences (Chem3D ) is 0.193 Å. The structure of one of the $Co(PMG)_2^{3-}$ anions is shown in Figure 4, with the water molecules and sodium atoms omitted for clarity. Selected bond lengths and angles are given in Table 3. Unlike the known 1:1 complexes with $Ca^{2+}$ and $Cu^{2+}$, glyphosate forms a monomeric 2:1 complex with $Co^{3+}$, acting as a tridentate ligand through the nitrogen, an oxygen of the carboxylate group, and an oxygen of the phosphonate group. Each ligating group is *trans* to the same group of the other ligand. This *all-trans* configuration represents the most symmetric molecule of all possible 2:1 isomers. The cobalt is in the center of an almost ideal octahedron with bond angles ranging from 87.5 (3) to 92.5(3)° [87.1(3) to 92.0(3)°]. Once bound to the metal, the nitrogen's stereochemistry is fixed. Since the configuration is *R* on one of the nitrogens and *S* on the other nitrogen, the idealized point symmetry of the $Co(PMG)_2^{3-}$ anion is $C_i$, implying an achiral molecule. As in the related compounds potassium *cis*-bis(iminodiacetato)chromate(III),[9] potassium *cis*-bis(iminodiacetato)cobaltate(III)[10] and dilithium *trans*-bis(iminodiacetato)nickelate(II),[11] both ligands form roughly perpendicular five-membered rings. The dihedral angle between the planes defined by Co1–N1–C1–P1–O1 and Co1–N1–C2–C3–O4 [Co2–N2–C4–P2–O6 and Co2–N2–C5–C6–O9] is 87.2° [80.6°]. The dihedral angles for the two molecules are similar to the corresponding angles for the related compound $K[Co\{HN(CH_2COO_2\}_2]$ (80.0°).[10] The rings involving N1 and C1 [N2 and C5] are puckered by up to 0.3 Å, while the rings involving N1 and C2 [N2 and C5] are planar within 0.05 Å [0.07 Å]. The cobalt–nitrogen distances and cobalt–oxygen distances (see Table 3) are within experimental error of the Co–N and Co–O distances in $K[Co\{HN(CH_2COO_2)\}_2]$ and are in agreement with those found for other Co(III) complexes.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for Compound 1

| | | | |
|---|---|---|---|
| Co1–O1 | 1.924(7) | P2–O8 | 1.524(8) |
| Co1–O4 | 1.919(7) | P2–C4 | 1.811(12) |
| Co1–N1 | 1.949(9) | O4–C3 | 1.287(12) |
| Co2–O6 | 1.922(7) | O5–C3 | 1.221(13) |
| Co2–O9 | 1.888(7) | O9–C6 | 1.296(13) |
| Co2–N2 | 1.953(9) | O10–C6 | 1.240(13) |
| P1–O1 | 1.561(8) | N1–C1 | 1.482(13) |
| P1–O2 | 1.503(8) | N1–C2 | 1.511(13) |
| P1–O3 | 1.512(8) | N2–C4 | 1.475(13) |
| P1–C1 | 1.795(13) | N2–C5 | 1.513(13) |
| P2–O6 | 1.544(7) | C2–C3 | 1.487(16) |
| P2–O7 | 1.509(8) | C5–C6 | 1.500(15) |
| O1–Co1–O4 | 89.5(3) | O3–P1–C1 | 109.2(5) |
| O1–Co1–O4 | 90.5(3) | O6–P2–O7 | 112.5(4) |
| O1–Co1–N1 | 89.3(3) | O6–P2–O8 | 110.4(5) |
| O1–Co1–N1 | 90.7(3) | O6–P2–C4 | 101.1(5) |
| O4–Co1–N1 | 87.5(3) | O7–P2–O8 | 113.0(5) |
| O4–Co1–N1 | 92.5(3) | O7–P2–C4 | 110.5(5) |
| O6–Co2–O9 | 91.7(3) | O8–P2–C4 | 108.8(5) |
| O6–Co2–O9 | 88.3(3) | Co1–O1–P1 | 117.2(4) |
| O6–Co2–N2 | 88.0(3) | Co1–O4–C3 | 114.5(8) |
| O6–Co2–N2 | 92.0(3) | Co2–O6–P2 | 118.0(4) |
| O9–Co2–N2 | 87.1(3) | Co2–O9–C6 | 115.0(7) |
| O9–Co2–N2 | 92.9(3) | Co1–N1–C1 | 108.8(7) |
| O1–P1–O2 | 110.9(5) | Co1–N1–C2 | 107.7(6) |
| O1–P1–O3 | 111.6(4) | C1–N1–C2 | 113.8(8) |
| O1–P1–C1 | 101.4(5) | Co2–N2–C4 | 108.4(7) |
| O2–P1–O3 | 113.7(5) | Co2–N2–C5 | 108.9(6) |
| O2–P1–C1 | 109.3(5) | C4–N2–C5 | 113.1(8) |

Formation of a 2:1 complex of glyphosate with Co(III) in the solid state, as opposed to the 1:1 complex favored by both Ca(II) and Cu(II), is ascribed to the higher charge and acidity of the cobalt(III) ion. The fact that charge plays a role in solid-state structure is supported by the symmetric distribution of negative charge about cobalt, with the formally dianionic phosphonate groups sitting *trans* to one another.

**NMR Results.** In the symmetric ($C_i$) and dissymmetric ($C_2$) isomers, both ligands are related by symmetry. This leads to an identical set of signals in the NMR spectra for each ligand. For the asymmetric isomers, one set of signals for each ligand is expected. The proton NMR spectrum of isomer **1** recorded in $D_2O$ at 500 MHz and 21 °C is shown in Figure 5. The diasterotopic protons of the $CH_2CO_2$ group occur as doublets at 4.34 and 3.77 ppm. The $J_{HH}$ coupling constant of 17.4 Hz is in the typical range for geminal coupling. The methylene protons of the $CH_2PO_3$ group appear as two doublets of doublets. Each doublet of the diastereotopic protons is further split by coupling with the phosphorus. Since the $J_{PH}$ and the $J_{HH}$ coupling

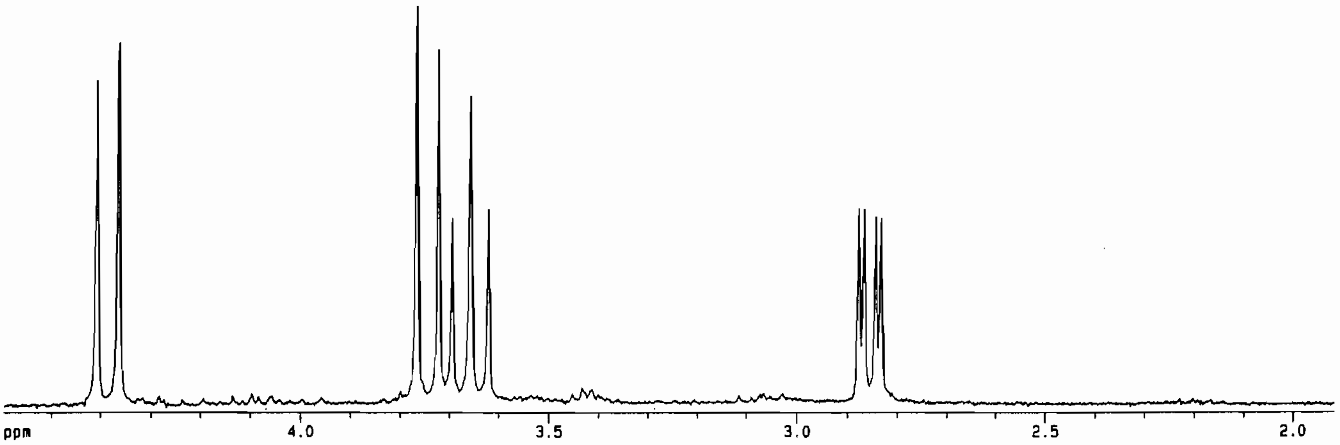

**Figure 5.** $^1$H-NMR spectrum of isomer **1** immediately after dissolving in $D_2O$.

constants are identical (14.5 Hz), the signal at 3.70 ppm appears as a pseudotriplet. The corresponding signal at 2.83 ppm shows a large $J_{HH}$ (13.8 Hz) and a small $J_{PH}$ (4.2 Hz) coupling constant. It is not clear why the diastereotopic protons of the $CH_2PO_3$ group show a large difference in the magnitude of their $J_{PH}$ coupling constants. As expected for the symmetric isomer **1**, only one signal appears in the $^{31}$P-NMR spectrum. The value of the chemical shift (40.7 ppm) is characteristic for phosphonate groups bound to a metal atom, where the phosphorus is part of a five-membered ring.[8] When the NMR spectrum of isomer **1** is not recorded immediately after dissolution, the peaks of the other isomers begin to appear. The process of isomerization is at equilibrium within 2 h (*vide infra*).

The $^1$H NMR (500 MHz), $^{31}$P NMR (400 MHz), and $^{13}$C NMR (400 MHz) spectra of this equilibrium mixture are shown in Figure 6. The complexity of the $^1$H NMR spectrum arises from the fact that the relatively simple spectra of the different compounds are overlapping. In order to detect corresponding peaks, especially those which are buried under other peaks, a 2D long-range $^1$H–$^1$H correlated spectrum was recorded (Figure 7). For example, two cross peaks are found for the doublet at 4.34 ppm, revealing that this signal consists of two doublets lying exactly on top of each other. The analysis of the COSY lead to 10 sets of doublets corresponding to the $CH_2CO_2$ protons and 10 sets of doublets of doublets corresponding to the $CH_2PO_3$ protons. This suggested the presence of 10 different glyphosate ligands in solution. However, at this point it was not possible to determine the number of $Na_3Co(PMG)_2$ isomers, since the asymmetric isomers would contain two nonsymmetry-related ligands. The $^1$H–$^1$H 2D-NOESY was thus recorded in order to find pairs of different ligands belonging to the same asymmetric isomers by observing the interactions through space (nOe) between protons of nonsymmetric related ligands. Unfortunately, the NOESY spectrum did not reveal any additional information, as the overlapping peaks prevented obtaining exact integration in several cases. Thus the assignment of the ligands to the asymmetric isomers is based only on estimated integrations and can not be done unambigously.

As expected, the $^{13}$C NMR spectrum contains 10 peaks in the carboxylate region indicating 10 different glyphosate ligands. Although this is consistent with the results discussed above, there are only 7 signals for the carbons of the $CH_2CO_2$ group and only two signals for the carbons of the $CH_2PO_3$ group. Even in the $^1$H–$^{13}$C 2D correlation experiment it was impossible to unambigously identify cross peaks because of the overlap of neighboring peaks. Cross peaks could only be identified in the carboxylate region (Figure 8).

Surprisingly, the $^{31}$P NMR spectrum of the equilibrium mixture shows more than 10 signals in the region 35–45 ppm. It is assumed that this is due to a very small amount of the complex in which one of the glyphosate ligands is only bidentate with an unbound carboxylate group. Such isomers would cause two signals in the region 35–45 ppm because of their $C_1$ symmetry, but those may not be detectable in the $^1$H-NMR or $^{13}$C-NMR spectra due to their low concentration. By the use of a $^1$H–$^{31}$P correlated spectrum (hetero COSY) it was possible to find the corresponding peaks for most of the 10 different ligands. The results of the different 1D and 2D experiments are listed in Table 4. The assignment of $^1$H NMR spectra for the different isomers is depicted schematically in Figure 9.

**Table 4.** $^1$H, $^{13}$C, and $^{31}$P NMR Chemical Shifts (ppm) and Coupling Constants (Hz) of the Different Isomers of $Na_3Co(PMG)_2$ in $D_2O$ at 21 °C

| isomer | $\mathit{CH_2}CO_2$[a] | $\mathit{CH_2}PO_3$[b] | $CH_2\mathit{CO_2}$[c] | $CH_2\mathit{PO_3}$[d] |
|---|---|---|---|---|
| **1** | 4.343/17.40 | 3.702/14.55/14.55 | 188.56 | 40.7 |
| | 3.776/17.45 | 2.826/13.85/4.20 | | |
| | [58.17/12.46] | [50.89/137] | | |
| **2** | 4.355/17.60 | 3.709/14.70/14.70 | 186.77 | 41.0 |
| | 3.805/17.35 | 2.804/14.70/4.15 | | |
| **3** | 3.938/16.55 | 3.054/14.15/9.80 | 187.25 | 37.7 |
| | 3.075/16.55 | 2.172/14.15/10.45 | | |
| | [59.84/4.90] | [58.17/12/46] | | |
| **4** | 4.110/17.85 | 2.866/14.10/9.10 | 187.73 | 36.9 |
| | {3.442} | {3.45} | | |
| **5** | 4.297/16.60 | 3.582/13.20/5.0 | 186.59 | |
| | 4.038/16.60 | {3.485} | | {39.2}[e] |
| | 4.264/16.40 | 3.567/12.60/5.18 | 186.73 | |
| | 4.006/16.40 | 3.436/13.15/13/15 | | |
| | | | | {39.4}[e] |
| **6** | 4.175/16.35 | 3.231/14.35/14.35 | 186.74 | 37.3 |
| | 3.990/16.60 | 2.232/13.88/4.58 | | |
| | 4.030/16.85 | 3.007/14.55/14.55 | 186.68 | 36.6 |
| | 4.123/16.20 | 2.260/14.35/4.68 | | |
| **7** | 4.024/16.90 | 2.122/13.80/11.30 | 187.66 | 38.9 |
| | {3.469} | | | |
| **8** | 3.853/16.65 | 2.232/13.80/4.58 | 186.74 | |
| | {3.033} | | | |

[a] Protons of the $\mathit{CH_2}CO_2$ are diasterotopic and each occurs as a doublet. $\mathit{CH_2}CO_2$ data reported as follows: $^1$H $\delta/J_{HH}$ and [$^{13}$C $\delta/J_{CH}$]. [b] Protons of the $\mathit{CH_2}PO_3$ group are diastereotopic and each occurs as a doublet of doublets. $\mathit{CH_2}PO_3$ data reported as follows: $^1$H $\delta/J_{HH}/J_{PH}$ amd [$^{13}$C $\delta/J_{PC}$]. [c] $^{13}$C shifts of the $CH_2\mathit{CO_2}$ carbonyl group. [d] $^{31}$P shifts of the $CH_2\mathit{PO_3}$ group. [e] Tentative assignments are given in braces.

**Time-Dependent NMR Spectra.** In order to follow the isomerization process, $^1$H NMR spectra of the freshly dissolved isomer **1** were recorded every 2 min in $D_2O$ at room temperature. To determine the amount of each isomer in solution at different times, a characteristic peak was observed and integrated relative to the DMSO integration standard. The integration of several peaks could only be obtained approximately by subtracting the known integration from the overlapping peak. Although no exact kinetic analysis could be obtained from these NMR measurements, it is possible to make some general conclusions about the isomerization mechanism.

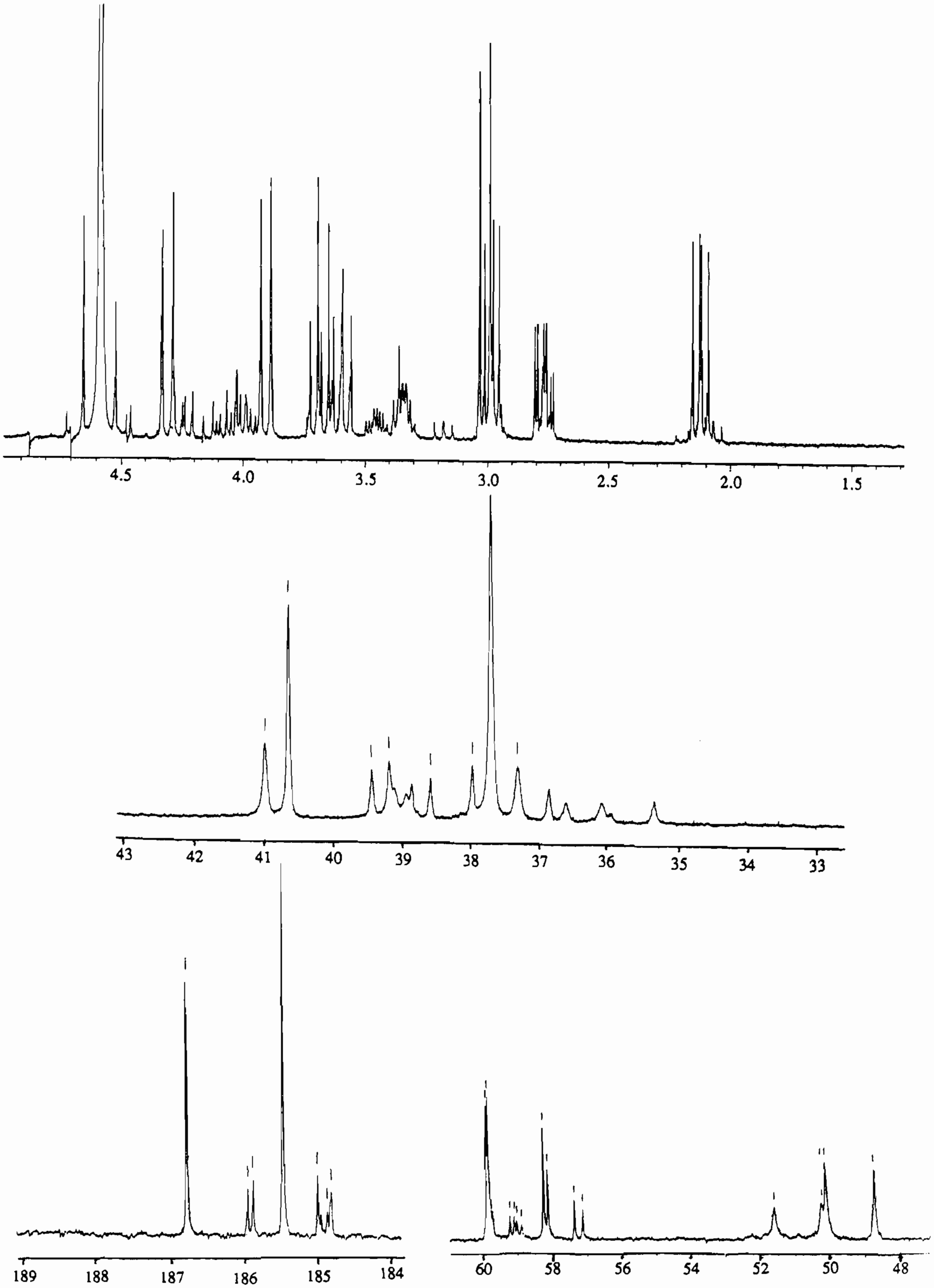

**Figure 6.** $^1$H-NMR spectrum (top), $^{31}$P-NMR (middle), $^{13}$C-NMR (bottom) of an equilibrium mixture of all isomers in $D_2O$ (δ in ppm).

The rate of isomerization of the *fac-RS-all-trans* isomer **1** to the other isomers is unexpectedly high for a Co(III) complex that should be kinetically inert. The increase of the concentration versus time is shown for the isomers **2**–**6** in Figure 10. The relative concentration of isomers **7** and **8** could not be determined due to their low concentrations and the strong overlap of the corresponding signals. The estimated rate constants can only be given for the isomerizations **1** → **5**, **1** → **6**, and **1** → **4** (see Table

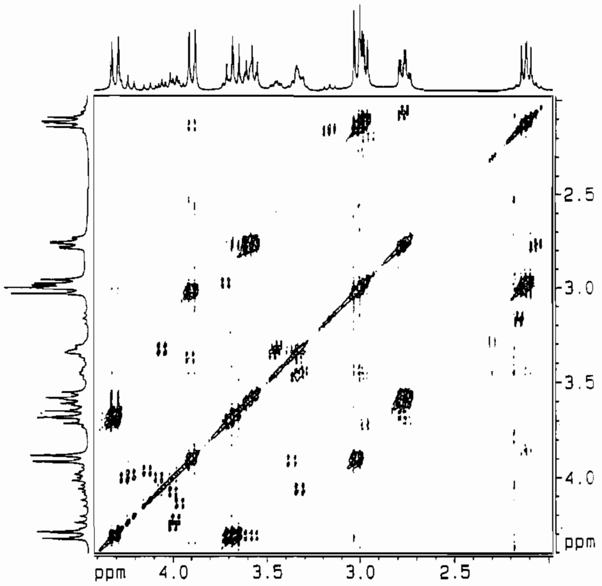

**Figure 7.** COSY ($^1H$–$^1H$) of an equilibrium mixture of $Na_3Co(PMG)_2$ in $D_2O$.

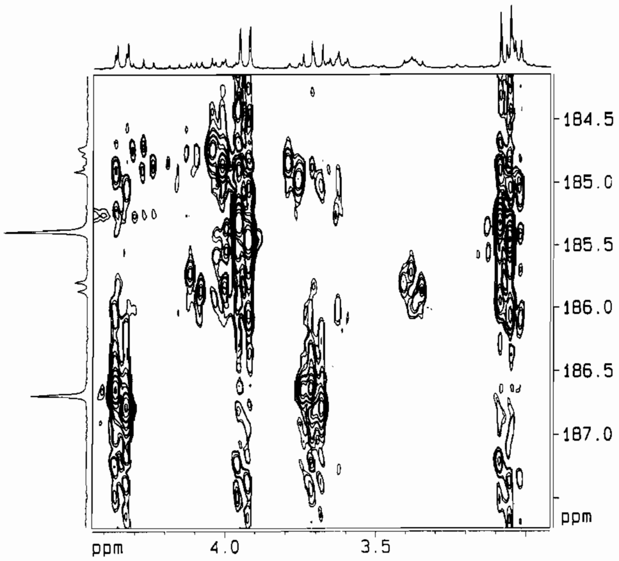

**Figure 8.** Heteronuclear COSY ($^1H$–$^{13}C$) of an equilibrium mixture of $Na_3Co(PMG)_2$ in $D_2O$.

5). These isomers show nearly exponential behavior in the increase of their concentrations. The rate constants $k_{ij}$ represent the formation of isomer *j* from the isomer *i*. The ratio $k_{ij}/k_{ji}$ represents the individual equilibrium constant $K_{ij}$. Since these equilibrium constants are known from the ratio of isomers, $k_{ji}$ is determined, if $k_{ij}$ is known. Isomers **5** and **6** show the highest initial rate constants with the steepest slopes at the very beginning of the reaction and no induction period at all. Since the concentration of isomer **1** is high at the beginning of the reaction, it is likely that isomers **5** and **6** are formed directly from isomer **1**. The concentration versus time plot of isomer **2** clearly shows an induction period, while isomer **3** seems to lie somewhere between showing an induction period and some immediate formation from isomer **1**. Isomer **4** shows some evidence of an induction period. Thus, it is likely that these isomers are formed from intermediates. We can make some isomer assignments from these observations since we expect that the isomerizations which do not require configurational changes at the ligand's nitrogen (**1** → **5**, **6**) are much faster than the isomerizations where the configuration at the nitrogen is inverted (**1** → any *RR* or *SS* isomer). Since the latter processes demand multiple bond cleavage, the activation barrier is high and the rate of formation slower. Thus, the concentration versus time plot shows induction periods for the isomers **2**–**4**. Each of the *RR* or *SS* isomers could be the intermediate for the formation of another *RR* or *SS* isomer.

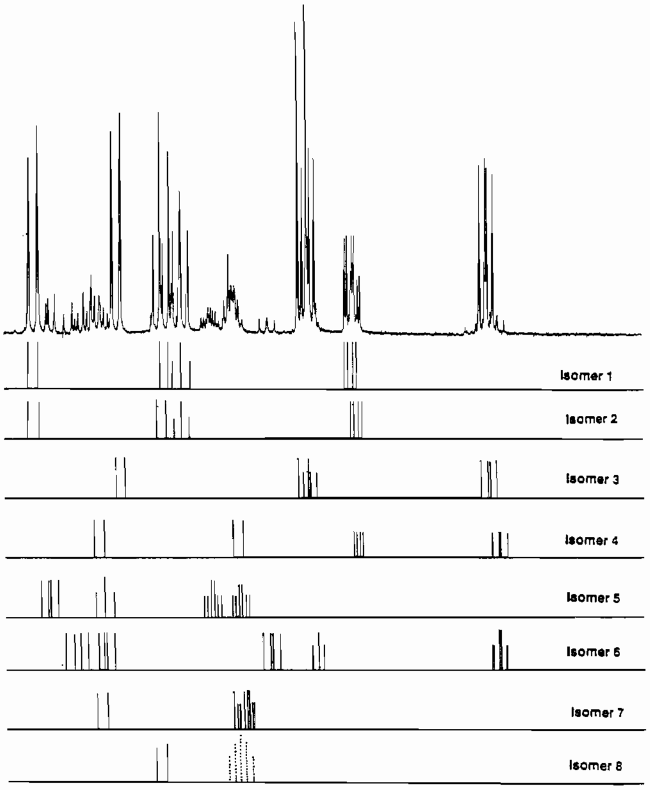

**Figure 9.** Schematic representation of the $^1H$-NMR spectra of the individual isomers.

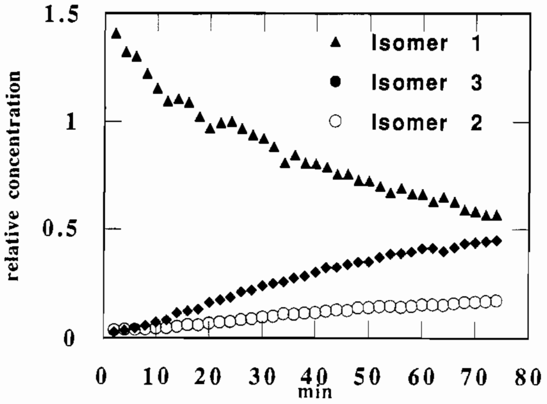

**Figure 10.** Plots of integrals **1**–**3** *vs* time. Integrations correspond to two protons for each individual isomer.

**Table 5.** Rate Constants of the Isomerization

| $k_{ij}$,[a] $min^{-1}$ | $K_{ij}$[b] |
|---|---|
| $k_{14} = 0.103$ | $K_{14} = 1.78$ |
| $k_{15} = 0.125$ | $K_{15} = 2.73$ |
| $k_{16} = 0.102$ | $K_{16} = 3.55$ |
| $k_{41} = 0.070$ | |
| $k_{51} = 0.046$ | |
| $k_{61} = 0.035$ | |

[a] $k_{ij}$ represents the rate of formation of isomer *j* from isomer *i*. [b] $K_{ij}$ represents the ratio of $k_{ij}/k_{ji}$.

A similar behavior has been observed for the related system $K[Co(Rida)_2]$ (Rida = alkyliminodiacetic acid), in which it was found that isomerization from the *fac-cis* isomer to the *fac-trans* isomer occurs through the *mer* isomers, which are in "preequilibrium" with the *cis* isomer.[14,15] For the isomerization itself, a "twist mechanism" through an antiprismatic complex and a bond rupture mechanism were discussed.

We suggest that the isomerizations without configurational changes take place through a high-spin intermediate, as for the ligand exchange in $[Co(H_2O)_6]^{3+}$. The hexaquo compound shows an "alarmingly" high rate of water exchange due to the low gap of only 4.2 kcal between the $d^6$ low-spin and the $d^6$ high-spin states.[16] The $d^6$ high-spin state labilizes the $H_2O$ ligands, making fast ligand exchange possible. For the $Co(PMG)_2^{3-}$ complex, the ligand field stabilization energy (LFSE) can be roughly estimated from those of $Co(H_2O)_6^{3+}$ (4.2 kcal) and $Co(NH_3)_6^{3+}$ (32.8 kcal). Since $Co(PMG)_2^{3-}$ is a complex of the $Co[N_2O_4]$ type, its LFSE can be estimated as ~14 kcal. This estimated energy gap would be identical with the activation energy for a ligand exchange process occuring through a $d^6$ high-spin intermediate, and is still low enough that the process can take place at room temperature.

A transition from $d^6$ low spin to $d^6$ high spin would cause an increase in the ionic radius of $Co^{3+}$. This allows the possibility of an associative interchange ($I_A$) mechanism in which addition of water to form a seven-coordinate species is the first step of the reaction. Once the complex is labilized by transition to the $d^6$ high-spin state isomerization could take place through different mechanisms including the Bailar-type[17] or Ray–Dutt-type twist mechanism.[18]

**Ratio of the Isomers.** The ratio of the isomers **1**:**2**:**3**:**4**:**5**:**6**:**7** in the equilibrium mixture was found to be 7.1:5.0:13.8:4.0:2.6: 2.0:1.0. The relative abundance of isomer **8** could not be determined due to the strong overlap of neighboring signals and its low concentration. The minor, and therefore less stable compounds, in the equilibrium mixture are believed to be meridional isomers. These isomers should be considerably more strained than the facial isomers. This aspect will be important later in the discussion of the tentative assignment of the isomers.

**UV Spectra.** For cobalt(III) complexes with a coordination sphere of two N,O,O ligands the VIS/UV spectra are diagnostic for the *cis* or *trans* configuration.[19-21] The *cis* isomers with respect to the nitrogens are expected to show two transitions; *trans* isomers should show three transitions. Theoretically, the $^1T_{1g}$ state should show a marked splitting in the *trans* isomer, since O and N ligating groups are substantially different in the spectrochemical series. Thus, a splitting of the transition at the lower wavelength side is expected for the *trans* isomers. This theoretical background was used to assign *trans* and *cis* isomer of the related compound $K[Co(IDA)_2]$.[22,23]

The UV spectrum of the equilibrium mixture in water shows three bands with absorption maxima at 397 and 528 nm and a shoulder at 620 nm. The UV spectrum of pure isomer **1** (*RS-fac-all-trans*) recorded in $H_2O$ shows three absorption maxima (see Figure 2 and Table 1) and is consistent with the *trans* configuration of the nitrogens as confirmed by the X-ray crystal structure. As mentioned above, only isomer **1** crystallizes from the equilibrium mixture of all isomers in water upon addition of a less polar solvent like ethanol or acetone. The remaining mother liquor contains predominantly isomer **3**, as shown by NMR spectroscopy, and has a somewhat different UV spectrum. The largest absorption band for isomer **3** is located at 604 nm, which is significantly higher than the absorption maximum, of about 520 nm, found for the *trans* isomer of $Na_3Co(PMG)_2$. The *cis* isomers of $K[Co(IDA)_2]$ and related compounds of the $N_2O_4$ type are also found to have absorption maxima at higher wavelengths than the corresponding *trans* isomers.[14,21-23] Thus, the major component in the blue mother liquor is assigned to a *cis* isomer. Dilution of the mother liquor with $H_2O$ causes an isomerization to the equilibrium mixture within 2 h, which can be followed by UV spectroscopy. The UV spectra taken at different times (Figure 11) indicate the isomerization is predominantly from isomer **3** to isomer **1**, although the lack of an isosbestic point indicates that an intermediate must occur for this process.

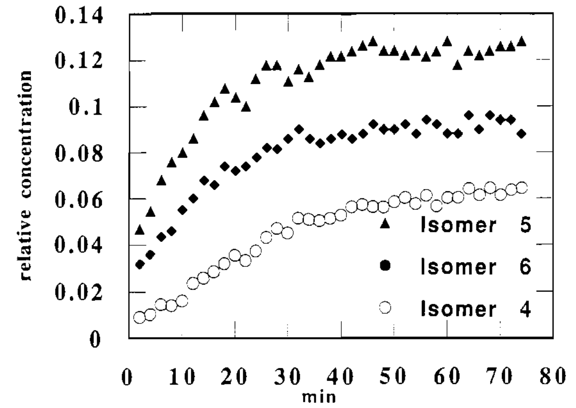

**Figure 11.** Plots of integrals for isomers **4**–**6** *vs* time. Integrations correspond to two protons for each individual isomer.

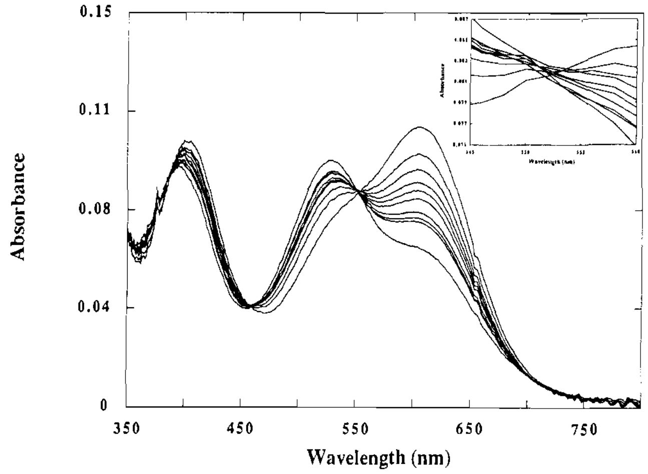

**Figure 12.** Plot of the UV spectral changes with time upon diluting the $EtOH/H_2O$ "blue mother liquor", which contains mainly isomer 3. The band at 604 nm decreases, while the band at 528 nm increases in intensity with time. Inset: "pseudo isosbestic point" at ~550 nm.

**Assignment of the Isomers.** Only the *fac-RS-all-trans* isomer **1** is achiral due to its $C_i$ symmetry. The other isomers are either dissymmetric ($C_2$ symmetry) or asymmetric ($C_1$ symmetry) and therefore chiral, in enantiomeric pairs. Centers of chirality are the nitrogens, in all isomers, and the metal atom in the *fac-cis* and *mer-trans* isomers. In the latter, the metal atom can adopt either a D or a L configuration. The nomenclature of the isomers in Figure 1 depicts the configuration of the metal atom and both nitrogens, followed by the position (*cis* or *trans*) of the nitrogen, phosphonate, and the carboxylate groups with respect to each other. The determination of D or L configurations for 2:1 complexes with a terdentate ligand has been explained for *mer* isomers in a previous paper.[23] Only isomer **1** could be obtained

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in a pure state, and was fully characterized as the asymmetric *fac-RS-all-trans* isomer. The assignment of the remaining isomers is based on the spectroscopic data and cannot be made unambigously. Isomer **2** shows almost the same chemical shifts and coupling constants as isomer **1**, and therefore is believed to be a racemic mixture of the *fac-trans-RR* and *fac-trans-SS* isomer. It should be noted that the **1**:**2** ratio is 1.42. The greater stability of **1** compared to **2** could be due to the *trans* position of the more highly charged phosphonate groups in isomer **1** compared to the *cis* position of the phosphonate groups in isomer **2**.

Isomer **3** is the major component of the equilibrium mixture. In the blue mother liquor from which isomer **1** crystallizes, isomer **3** becomes the predominant species and was identified as a *cis* isomer by its absorptions in the UV spectrum. Since isomer **3** shows only one set of signals for both glyphosate ligands in the NMR spectrum, the ligands must be related by $C_2$ symmetry. Therefore, the *all-cis-ΛRS* and *ΔRS* isomers **5**, which have $C_1$ symmetry, can be excluded. Using the same stability argument as that employed for the *fac-trans* isomers, we assume that isomer **3** is the racemic mixture of the *fac-cis-ΔRR* and *fac-cis-ΛSS* isomers which have $C_2$ symmetry and the phosphonate groups in a *trans* positon. Isomer **4** also has $C_2$ symmetry and could be the *fac-cis-ΛRR* and *fac-cis-ΔSS* isomers with the phosphonate groups in a *cis* position, from which its smaller stability compared to isomer **3** (ratio isomer **3** to isomer **4** = 3.45) should arise.

Isomer **5** is believed to be the racemic mixture of the asymmetric *fac-all-cis-ΔRS* and *fac-all-cis-ΛRS* isomers. This is consistent with its NMR spectrum, which shows two sets of signals for each glyphosate ligand. The other possibility to be considered is that isomer **5** is the mixture of the *mer-trans-ΔRS* and *mer-trans-ΛRS* isomers, which are also asymmetric. This possibility was discounted, since the relative abundance of isomer **5**, and therefore its thermodynamic stability, is higher compared to that of isomer **6**. Thus isomer **5** should be a *fac* isomer which is less strained than a *mer* isomer.

Since isomers **6**–**8** are minor compounds in the equilibrium mixture, they are believed to be *mer* isomers. Because of the steric constraints of the ligand, they should be considerably less stable than the *fac* isomers. From symmetry considerations, isomer **6** was assigned to the racemic mixture of *mer-trans-ΔRS* and *mer-trans-ΛRS* isomers (both $C_1$ symmetry). Isomers **7** and **8** were assigned to be the *mer-trans-ΔRR* (*mer-trans-ΛRR*) and the *mer-trans-ΔSS* (*mer-trans-ΛSS*) respectively. However, it is not possible to distinguish between isomers **7** and **8**.

**Chromium Complexes.** The chromium complex was characterized only by its mass spectrum and its UV spectrum. The UV spectrum shows two absorption maxima at 412 and 562 nm, which is consistent with a *fac cis* isomer. This is expected, since the complex was obtained from a reaction where $CrCl_3$ was heated with glyphosate in water for 30 min, from which it is expected that the thermodynamically most stable product is formed. Assuming that the stabilities of the cobalt isomers are similar to the chromium isomers, the most stable isomers would be the racemic mixture of the *fac-cis-ΔRR* and *-ΛSS* isomers, where the phosphonate groups are standing *trans* to each other. The mass spectrum contains the parent ion peak, as well as other species with higher masses. Although only two absorption bands are detected in the UV spectrum, it cannot be ruled out that other 2:1 species of the chromium complex are present in solution in low concentration. This is in analogy to the three absorption bands due to the absorptions of different isomers seen in the UV spectrum of the cobalt complex.

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**Supplementary Material Available:** X-ray crystallographic data are available for $Co(PMG)_2$ (**1**), including tables of anisotropic thermal parameters, atom positional parameters, non-essential intramolecular distances and angles, and Chem3D minimized individual atomic deviations for the two crystallographically independent $Co(PMG)_2$ molecules (9 pages). Ordering information is given on any current masthead page.