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Spin-Crossover Cobalt(III) Complexes: Steric and Electronic Control of Spin State

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The preparation of the series of octahedral cobalt(III) spin-crossover complexes $[CoL_2]^+$ is described where the ligands L^- = $[(C_5H_5)Co\{P(O)R_2\}_3]^-$, with R = OCH_3, OC_2H_5, $OCH(CH_3)_2$, $OCH_2CH_2CH_2CH_3$, $OCH_2C(CH_3)_3$, C_2H_5, $CH_2C_6H_5$, act as oxygen tripod ligands. Depending on the steric and electronic effects of the substituents R, a systematic fine tuning of the magnetic behavior, at a given temperature, from essentially high spin over spin equilibrium to completely diamagnetic can be achieved. The paramagnetic complexes are dark green; the diamagnetic complexes are yellow. The magnetic susceptibilities of the spin-crossover complexes in the solid state have been measured in the temperature range 4.2–320 K and in solution at 300 K. The spin transition in solution is fast on the NMR time scale, and the equilibrium can be described by a Boltzmann distribution between the high-spin and the low-spin state. The thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ of the low-spin to high-spin transition have been determined from variable-temperature (170–330 K) ^{31}P NMR spectra. The ligand field spectra of the transition-metal complexes ML_2, M = Co(II), Ni(II), Cu(II), characterize L^- as very hard ligands whose position in the spectrochemical series is near that of fluoride. The variation of the substituents R in the ligands L^- causes a small variation in ligand field strength in the order R = $C_2H_5 > OCH_3 \approx OC_2H_5 \approx OCH_2CH_2CH_2CH_3 > OCH(CH_3)_2$. This is in accord with the observed hs/ls ratio at 300 K in the opposite order R = $OCH(CH_3)_2 \gg OCH_2CH_2CH_2CH_3 \geq OC_2H_5 \geq OCH_3 \gg C_2H_5$ as determined from the ^{31}P NMR spectra. The cause of the observed influence of the substituents R = alkoxy on the spin equilibrium position is very probably increasing interligand repulsion as the substituents become more bulky.

Introduction

The first examples of metal complexes exhibiting spin equilibria between low-spin (ls) and high-spin (hs) electronic ground states were described by Cambi and his co-workers in 1931.[2] Since then a number of other spin-crossover systems have been found. One can expect spin-crossover behavior in octahedral complexes in principle with the configurations d^4, d^5, d^6, and d^7. The experimental realization of such an equilibrium is confined, however, to compounds for which the energy difference between the low-spin and high-spin ground states is in the range of kT. This requirement is very restrictive and explains why only a few classes of transition-metal complexes have been found to exhibit hs–ls equilibria. Of the d^6 ions only iron(II) spin-crossover complexes are well documented.[3] What about the other d^6 ions? Vanadium(–I), chromium(0), manganese(I), and nickel(IV) all form low-spin complexes exclusively. The vast majority of octahedral cobalt(III) complexes are also low spin; even the cobalt(III) aquo ion is a low-spin species. The only exceptions are the high-spin complexes $[CoF_6]^{3-}$[4] and $[CoF_3(H_2O)_3]$.[5]

In the search for cobalt(III) spin-crossover compounds one has thus to look for very hard ligands whose position in the spectrochemical series is between those of water and fluoride. Most of the ligands that would fulfill these requirements however are not stable toward the high oxidizing power of the cobalt(III) ion. We have recently described the synthesis of a new class of anionic trischelating oxygen ligands[6–8] that are about as weak as fluoride and whose position in the nephelauxetic series is near that of water.[7] The schematic structure of this type of ligand **1**, hereafter abbreviated as L^-, is shown in Figure 1. These anionic ligands are diamagnetic and very inert toward hydrolysis and oxidizing agents.

The complex $[CoL_2]^+$, R = OC_2H_5, is the first reported example of an octahedral spin-crossover cobalt(III) complex.[9] The temperature dependence of the hs–ls equilibrium in solution has been studied by ^{31}P NMR,[10] UV–vis, and ^{59}Co NMR spectroscopy.[11]

We have now found that by variation of the steric and electronic effects of the substituents R in the complexes $[CoL_2]^+$ a systematic fine tuning of the magnetic behavior, at a given temperature, from essentially high spin over spin equilibrium to completely diamagnetic can be obtained.[12]

Experimental Section

Dimethyl phosphite (Bayer Leverkusen), diethyl phosphite (Bayer Leverkusen), diisopropyl phosphite (Fluka), and dibutyl phosphite (Fluka) were used without further purification. Dicyclopentadienylcobalt,[13] tris(*p*-bromophenyl)aminium hexachloroantimonate[14] and the oxygen tripod compounds **1b**, sodium salt,[6] **1f**, sodium salt,[8] **2a,b**,[15] **2f,g**,[8] **3a,b** and **4a,b**,[7] and **5b**[16] were prepared according to the published procedures. Dicyclopentadienylcobalt was freshly sublimed prior to use and handled under an atmosphere of dry nitrogen in Schlenk glassware. The elemental analyses were obtained from Analytical Laboratories, D-5250 Engelskirchen, ^1H and ^{13}C NMR spectra were recorded on Bruker WP 80 and WH 270 spectrometers. Variable-temperature (170–330 K) ^{31}P NMR spectra of the spin-crossover complexes in dichloromethane and acetone solutions were measured on a Bruker WH 90 instrument. ^{31}P chemical shifts are given relative to external 85% H_3PO_4. Infrared spectra were recorded on Perkin Elmer PE 457 and 580 spectrometers and ligand field spectra (UV–vis and near-IR) on PE 330 and PE 340 spectrometers. The magnetic susceptibilities of the spin-crossover complexes in dichloromethane solution were determined by the Evans method[17] with 1% *tert*-butyl alcohol as reference. Variable-temperature ($4.2 \leq T \leq 320$ K) magnetic susceptibility measurements on powdered samples were carried out with a Foner type[18] vibrating-sample magnetometer equipped with a conventional electromagnet (Bruker, ≤20 kOe, homogeneity better than $1:10^5$) and a commercial vibrator (PAR). The samples were thermostated in a helium flow cryostat (CryoVac, Troisdorf, FRG) and temperature-controlled to within ±0.05 K by using a thermocouple (Au with 0.03% Fe vs Ni with 10% Cr, Degussa), which was calibrated with a reference silicon diode (LAKE SHORE type DT-500 P). The magnetometer was calibrated with high-purity nickel at room temperature (55.01 emu/g).[19] The measured susceptibility of the standard material $Hg[Co(SCN)_4]$ (literature value 16.44 emu/g)[20]

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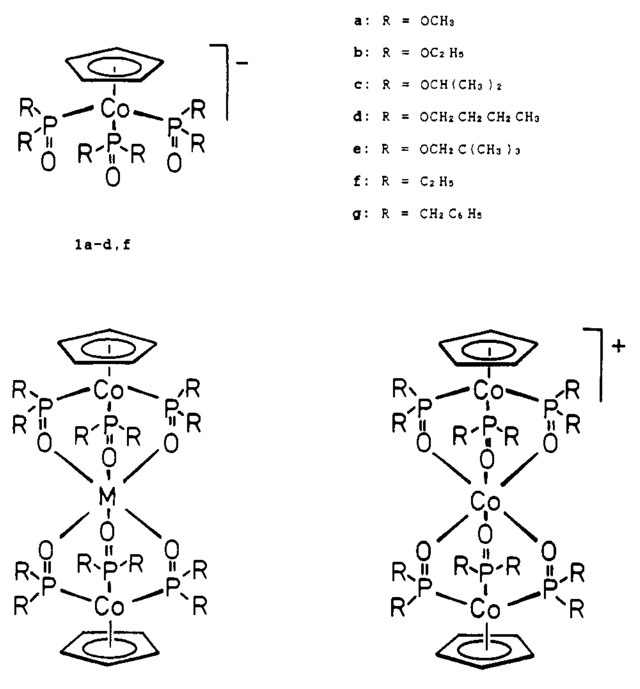

1a-d,f

2a-g: M = Co(II)

3a-d,f: M = Ni(II)

4a-d,f: M = Cu(II)

5a-g

Figure 1. Schematic structures of the oxygen tripod ligands L^- and their metal complexes.

yielded 16.43 emu/g at room temperature. Samples of approximately 20 mg were weighted into a "Spectrosil" container (free of paramagnetic impurities) and measured at a field of 10 kOe. No field dependence was observed for the present compounds. The data were corrected for diamagnetic contributions arising from both the sample holder and the ligand material, by measuring their susceptibilities separately at different temperatures.

Dineopentyl Phosphite.[21] A mixture of 2,2-dimethylpropanol (17.6 g, 0.2 mol) and methanol (3.2 g, 0.1 mol) was added dropwise with vigorous stirring to ice-cooled phosphorus trichloride (13.7 g, 0.1 mol). Chloromethane evolved, which was removed at reduced pressure. Heating to 80 °C for 20 min removed the last traces of hydrogen chloride. The yield was 18.5 g (83%) of a viscous, colorless oil. IR (cm^{-1}, film): 2420 m (ν(P—H)), 1257 vs (ν(P=O)). ^1H NMR (δ, 60 MHz, CCl_4/benzene-d_6): 0.9 (s, 18, CH_3), 3.7 (d, 4, CH_2, ^3J(POCH) = 3.5 Hz), 6.1 (d, 1, PH, ^1J(PH) = 606 Hz).

Sodium Cyclopentadienyltris(dimethyl phosphito-*P*)cobaltate(1−) (1a, Sodium Salt). A suspension of **2a** (5.75 g, 6.0 mmol) and NaCN (2.02 g, 41.2 mmol) in methanol (ca. 50 mL) was stirred in air for 12 h. The yellow solution was pumped to dryness at reduced pressure, and the brown residue was extracted with ether by means of a Soxhlet extractor. Evaporation of the solvent yielded 2.67 g (47%) of yellow crystals. IR and ^1H NMR spectra are identical with those of **1a** prepared via a different route.[7]

Sodium Cyclopentadienyltris(diisopropyl phosphito-*P*)cobaltate(1−) (1c, Sodium Salt). A suspension of **2c** (57.8 g, 44 mmol) and NaCN (25 g, 0.5 mol) in methanol (ca. 400 mL) was stirred in air for 5 days. The solvent was removed at reduced pressure, and the yellow residue was dried under high vacuum. Soxhlet extraction with hexane/ether (1:3) was used to remove insoluble NaCN and $Na_3[Co(CN)_6]$. Evaporation of the solvent yielded a yellow powder. This was extracted with three portions of 200 mL of pentane. The combined solutions were filtered to remove a small amount of unreacted **2c**. The yield after evaporating and drying under high vacuum was 42.5 g (66.1 mmol, 75%) of a yellow powder. ^1H NMR (δ, 80 MHz, $CDCl_3$): 1.23 and 1.25 (2 d, 36, POCH(CH_3)$_2$, ^3J(HCCH) = 6.2 Hz), 4.6–5.0 (m, 6, POCH), 4.9 (s, 5, C_5H_5). $^{13}C\{^1H\}$ NMR (δ, 67.88 MHz, $CDCl_3$): 24.6 (s, br, POCH(CH_3)$_2$, 65.9 (virtual q, POCH, ^2J(POC) = 9.5 Hz), 90.1 (q, C_5H_5, ^2J(PCoC) = 1.7 Hz). ^{13}C NMR (δ, 67.88 MHz, $CDCl_3$): 24.6 (d·q, br, POCH(CH_3)$_2$, ^1J(CH) = 125.5 Hz), 65.9 (d, br, POCH, ^1J(CH) = 145.3 Hz), 90.1 (d·p·q, C_5H_5, ^1J(CH) = 179.7 Hz, ^2J(HCC) and ^3J(HCCC) = 6.9 Hz). Anal. Calcd for $C_{23}H_{47}CoNaO_9P_3$: C, 43.00; H, 7.37; Co, 9.17; Na, 3.58. Found: C, 43.10; H, 7.39; Co, 9.07; Na, 3.79.

Sodium Cyclopentadienyltris(dibutyl phosphito-*P*)cobaltate(1−) (1d, Sodium Salt). A mixture of 5.50 g (3.75 mmol) of **2d** and 1.23 g (25.1 mmol) of NaCN in 50 mL of methanol was stirred for 12 h. The solvent was removed at reduced pressure, and the solid residue was extracted with a minimum amount of CCl_4. Evaporation of the solvent and drying under high vacuum for several days yielded 4.18 g (5.75 mmol, 77%) of yellow waxy crystals. The sodium salt is insoluble in water but very soluble in all organic solvents. Isolation from hydrocarbon solvents tends to give viscous oils, which are difficult to crystallize. ^1H NMR (δ, 80 MHz, CD_3COCD_3): 0.8–1.0 (m, 18, CH_3), 1.2–1.7 (m, 24, $POCH_2CH_2CH_2$), 3.8–4.0 (m, 12, $POCH_2$), 5.0 (q, 5, C_5H_5, ^3J(PCoCH) = 0.5 Hz). $^{13}C\{^1H\}$ NMR (δ, 67.88 MHz, CD_3COCD_3): 14.3 (s, CH_3), 20.1 (s, CH_2CH_3), 34.1 (virtual q, $POCH_2CH_2$, ^3J(POCC) = 5.7 Hz), 63.3 (virtual q, $POCH_2$, ^2J(POC) = 8.6 Hz), 89.9 (s, C_5H_5). ^{13}C NMR (δ, 67.88 MHz, CD_3COCD_3): 14.3 (q·m, CH_3, ^1J(CH) = 123.9 Hz), 20.1 (t·m, CH_2CH_3, ^1J(CH) = 127.8 Hz), 34.1 (t·m, $POCH_2CH_2$, ^1J(CH) = 124.9 Hz), 63.3 (t·m, $POCH_2$, ^1J(CH) = 144.9 Hz), 89.9 (d·m, C_5H_5, ^1J(CH) = 178.3 Hz). Anal. Calcd for $C_{29}H_{59}CoNaO_9P_3$: C, 47.94; H, 8.18; Co, 8.11; Na, 3.16. Found: C, 47.91; H, 7.86; Co, 8.05; Na, 3.12.

Bis[cyclopentadienyltris(diisopropyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(II) (2c). Dicyclopentadienylcobalt (31 g, 164 mmol) and diisopropyl phosphite (60.5 g, 364 mmol) were heated together for 4 h to 150 °C. The cooled reaction mixture was stirred with 150 mL of methanol for 30 min. The air-stable orange crystals were filtered off, washed with a small amount of methanol and acetone, and dried under high vacuum. The yield after recrystallization from ether with a Soxhlet extractor was 59.8 g (46.1 mmol, 84%) of orange crystals. Anal. Calcd for $C_{46}H_{94}Co_3O_{18}P_6$: C, 42.57; H, 7.30; Co, 13.62. Found: C, 42.58; H, 7.19; Co, 13.69.

Bis[cyclopentadienyltris(dibutyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(II) (2d). Dicyclopentadienylcobalt (5.7 g, 30.0 mmol) and dibutyl phosphite (12.0 g, 61.8 mmol) were heated to 160 °C for 7 h without solvent. The resulting black slurry was cooled to room temperature. Addition of 25 mL of methanol afforded an orange air-stable precipitate, which was filtered off, washed with methanol, and dried. Purification by Soxhlet extraction with ether gave 11.4 g (7.7 mmol, 75%) of yellow waxy crystals. Anal. Calcd for $C_{58}H_{118}Co_3O_{18}P_6$: C, 47.51; H, 8.11; Co, 12.06. Found: C, 47.32; H, 8.13; Co, 11.63.

Bis[cyclopentadienyltris(dineopentyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(II) (2e). Dicyclopentadienylcobalt (2.8 g, 15 mmol) and dineopentyl phosphite (6.7 g, 30 mmol) were heated to 100 °C for 3 h without solvent. The dark brown viscous mixture was stirred with 30 mL of methanol to give a red-brown solution and an ocher precipitate. The precipitate was washed several times with methanol, water, and finally acetone. The yield after drying under high vacuum was 6.2 g (3.8 mmol, 76%) of light yellow fine crystals. The compound is only very slightly soluble in dichloromethane and insoluble in most other organic solvents. Anal. Calcd for $C_{70}H_{142}Co_3O_{18}P_6$: C, 51.44; H, 8.76; Co, 10.82. Found: C, 51.09; H, 9.04; Co, 10.46.

General Procedure for the Preparation of Bis[cyclopentadienyltris(diisopropyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]metal(II) (3c, 4c) and Bis[cyclopentadienyltris(dibutyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]metal(II) (3d, 4d). The sodium salts of the ligands **1c** and **1d** were dissolved in aqueous methanol. Addition of nickel(II) or copper(II) salts caused immediate formation of the yellow insoluble metal complexes, which were separated by centrifugation. The products were washed with water, dried under high vacuum, and recrystallized from tetrachloromethane/ether.

3c: from 286 mg (0.45 mmol) of **1c**, sodium salt, and 52 mg (0.22 mmol) of $NiCl_2 \cdot 6H_2O$; yield 248 mg (0.19 mmol, 86%). Anal. Calcd for $C_{46}H_{94}Co_2NiO_{18}P_6$: C, 42.58; H, 7.30. Found: C, 42.65; H, 7.04.

4c: from 532 mg (0.83 mmol) of **1c**, sodium salt, and 100 mg (0.41 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$; yield 476 mg (0.37 mmol, 88%). Anal. Calcd for $C_{46}H_{94}Co_2CuO_{18}P_6$: C, 42.42; H, 7.27; Cu, 4.88. Found: C, 42.13; H, 7.33; Cu, 4.75.

3d: from 588 mg (0.81 mmol) of **1d**, sodium salt, and 90 mg (0.38 mmol) of $NiCl_2 \cdot 6H_2O$; yield 484 mg (0.33 mmol, 81%). Anal. Calcd for $C_{58}H_{118}Co_2NiO_{18}P_6$: C, 47.52; H, 8.11. Found: C, 47.29; H, 7.96.

4d: from 602 mg (0.83 mmol) of **1d**, sodium salt, and 100 mg (0.41 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$; yield 547 mg (0.39 mmol, 94%). Anal. Calcd for $C_{58}H_{118}Co_2CuO_{18}P_6$: C, 47.36; H, 8.09; Cu, 4.32. Found: C, 47.28; H, 8.15; Cu, 4.31.

Bis[cyclopentadienyltris(diethylphosphinito-*P*)cobalt-*O*,*O*′,*O*″]nickel(II) (3f). $NiCl_2 \cdot 6H_2O$ (247 mg, 1.04 mmol) was added to a hot saturated solution of **1f**, sodium salt (1.00 g, 2.16 mmol in ca. 2 mL of water). The

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(21) Prepared according to a general procedure reported by: Mandel'baum, Ya. A.; Itskova, A. L.; Mel'nikov, N. N. *Khim. Org. Soedin. Fosfora* USSR Nonserial: Moscow, 1967; p 288; *Chem. Abstr.* **1968**, *69*, 43338h.

Table I. Magnetic Moments of the Cobalt(III) Complexes **5a–e** Measured by the Evans Method in Dichloromethane Solution at ca. 300 K and the hs/ls Ratios (Assuming $\mu_{eff} \approx 5.4\ \mu_B$ for the High-Spin Species)

	5a	5b	5c	5d	5e
μ_{eff}/μ_B	1.6	2.3	4.3	2.2	4.4
K = hs/ls	0.10	0.22	1.8	0.21	2.1
% high spin	12	18	64	17	68

voluminous precipitate was filtered off in the cold, washed with a small amount of water, and dried under high vacuum. Recrystallization from dichloromethane/ether afforded 390 mg (0.42 mmol, 39%) of orange octahedral crystals. The product is slightly soluble in water and hydrocarbon solvents and very soluble in chlorinated solvents, acetone, and methanol.

Bis[cyclopentadienyltris(diethylphosphinito-*P*)cobalt-*O*,*O*′,*O*″]copper(II) (4f). The compound was prepared in the same manner as for **3f** from 1.00 g (2.16 mmol) of **1f**, sodium salt, and 270 mg (1.08 mmol) of $CuSO_4 \cdot 5H_2O$; the yield was 353 mg (0.37 mmol, 35%) of yellow needles.

Bis[cyclopentadienyltris(dimethyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) Hexachloroantimonate (5a, $SbCl_6$ Salt). A blue solution of the radical $[(p\text{-}BrC_6H_4)_3N]SbCl_6$ (844 mg, 1.03 mmol) was added to a solution of the cobalt(II) complex **2a** (1.04 g, 1.08 mmol) in dichloromethane. The resulting dark green solution was filtered after ca. 1 h and concentrated at reduced pressure to 5 mL. The solvent was then slowly replaced by tetrachloromethane. A dark green precipitate formed, which was filtered off, washed with tetrachloromethane and methanol, and finally dried under high vacuum. The yield was 1.26 g (0.97 mmol, 90%) of light green crystals, which turn light yellow at −80 °C.

Bis[cyclopentadienyltris(diisopropyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) Hexachloroantimonate (5c, $SbCl_6$ Salt). The compound was prepared in the same manner as for **5a** from 1.00 g (0.77 mmol) of **2c** and 629 mg (0.77 mmol) of $[(p\text{-}BrC_6H_4)_3N]SbCl_6$; yield, 1.06 g (0.65 mmol, 84%) of dark green crystals.

Bis[cyclopentadienyltris(dibutyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) hexachloroantimonate (5d, $SbCl_6$ salt) was prepared in a similar manner as for **5a** from 1.00 g (0.68 mmol) of **2d** in 20 mL of dichloromethane and 557 mg (0.68 mmol) of $[(p\text{-}BrC_6H_4)_3N]SbCl_6$ in 20 mL of dichloromethane. The solvent was replaced by dibutyl ether, and the dark green precipitate was washed with methanol and pentane; yield 833 mg (0.46 mmol, 68%).

Bis[cyclopentadienyltris(dineopentyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) hexachloroantimonate (5e, $SbCl_6$ salt) was prepared in the same manner as for **5a** from 1.37 g (0.84 mmol) of **2e** and 668 mg (0.82 mmol) of $[(p\text{-}BrC_6H_4)_3N]SbCl_6$; yield 1.17 g (0.59 mmol, 71%) of dark green crystals.

Bis[cyclopentadienyltris(diethylphosphinito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) Hexachloroantimonate (5f, $SbCl_6$ Salt). A solution of $[(p\text{-}BrC_6H_4)_3N]SbCl_6$ (442 mg, 0.54 mmol, in 20 mL of dichloromethane) was added to a solution of **2f** (562 mg, 0.60 mmol, in 20 mL of dichloromethane). The product precipitated from the solution. It was washed with dichloromethane and dried under high vacuum. The yield was 189 mg (0.15 mmol, 25%) of light brown crystals. The product is insoluble in most organic solvents and only very slightly soluble in acetone.

Bis[cyclopentadienyltris(diethylphosphinito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) Hexafluorophosphate (5f, PF_6 Salt). A solution of **2f** (500 mg, 0.53 mmol, in 10 mL of dichloromethane) was slowly added to an equimolar amount of $[(p\text{-}BrC_6H_4)_3N]PF_6$. $[(p\text{-}BrC_6H_4)_3N]PF_6$ was freshly prepared from 135 mg (0.53 mmol) of $AgPF_6$ and 256 mg (0.53 mmol) of $[(p\text{-}BrC_6H_4)_3N]$ in 10 mL of dichloromethane. The light brown reaction mixture was stirred for 30 min and then filtered through Celite to remove silver. The solvent was slowly replaced by tetrachloromethane. A fine yellow-brown precipitate formed, which was recrystallized from acetone/ether; yield 455 mg (0.42 mmol, 79%) of yellow crystals.

Bis[cyclopentadienyltris(dibenzylphosphinito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) hexachloroantimonate (5g, $SbCl_6$ salt) was prepared in the same manner as for **5f**, $SbCl_6$ salt, from 504 mg (0.30 mmol) of **2g** and 253 mg (0.31 mmol) of $[(p\text{-}BrC_6H_4)_3N]SbCl_6$; the yield was 232 mg (0.11 mmol, 38%) of nearly insoluble fine yellow crystals. The corresponding hexafluorophosphate salt is also only very slightly soluble in organic solvents.

Results

The cobalt(III) complexes $[CoL_2]^+$ (**5a–g**) were synthesized from the corresponding cobalt(II) complexes **2a–g** by oxidation with the tris(*p*-bromophenyl)aminium radical cation[14] and isolated as hexafluorophosphate or hexachloroantimonate salts.

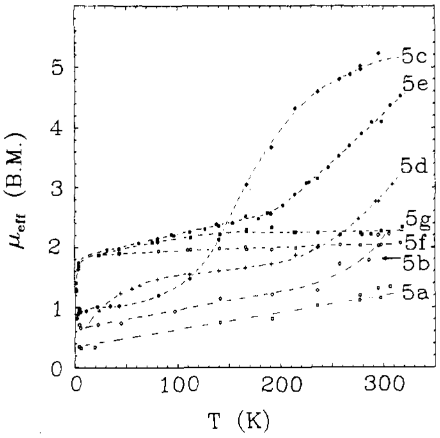

Figure 2. Effective magnetic moment $\mu_{eff}(T)$ as a function of temperature of the solid cobalt(III) complexes **5a–g**.

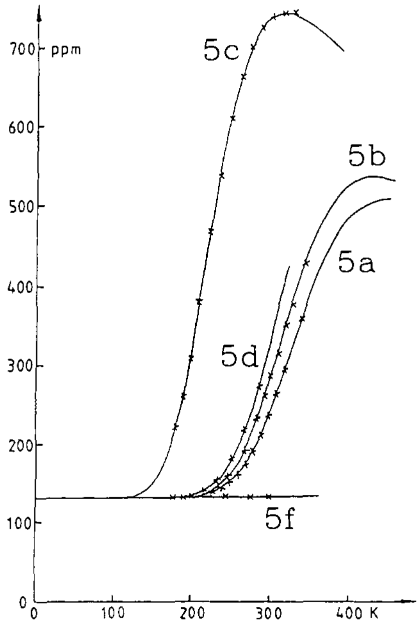

Figure 3. Temperature-dependent ^{31}P NMR chemical shifts of the cobalt(III) complexes **5a–d,f** in CD_2Cl_2/CD_3COCD_3: (×) experimental values; (—) calculated from eq 1.

The solid-state magnetism of the complexes **5a–g** as a function of temperature is shown in Figure 2. The effective magnetic moment (μ_{eff}) of the two complexes **5f** and **5g** with R = alkyl is approximately 2 μ_B and practically independent of temperature over the whole range of 320–10 K. There is no indication for spin-crossover behavior in these complexes. The compounds with R = O-alkyl, however, all show increasing effective magnetic moments with increasing temperature. Thus, they seem to form a class of spin-crossover complexes, but with varying tendencies of ls $\rightleftharpoons$ hs transition. At room temperature, the paramagnetic behavior dominates in **5c** and decreases in the order **5c** > **5e** > **5d** > **5b** > **5a**. The $\mu_{eff}(T)$ function for **5c** reaches a plateau around 5 μ_B, which is typical for a d^6-hs configuration with four unpaired electrons.

In solution the compounds with R = O-alkyl (**5a–e**) are paramagnetic and green at room temperature. They become diamagnetic and yellow at temperatures below −30 to −80 °C. The change in magnetism and the thermochromism are completely reversible. The compounds with R = alkyl (**5f,g**), however, are diamagnetic and yellow over the whole temperature range. The temperature dependence of the magnetism in solution can be adequately described by assuming a Boltzmann distribution between the high-spin and the low-spin state. It has been studied by NMR spectroscopy (see Figure 3). The signal of the six isochronous phosphorus nuclei in the complexes **5a–d** has been found to be very sensitive to the paramagnetism. The shift range as a function of temperature is nearly 600 ppm. The ^{31}P NMR signal of the diamagnetic complex **5f** is temperature-independent.

To understand the strong influence of the substituents R on the spin equilibrium position, we have studied the ligand field spectra of the cobalt(II), nickel(II), and copper(II) complexes containing the ligands L^- (**1a–d,f**). The ligand field strength decreases along the series R = $C_2H_5 > OCH_3 \approx OC_2H_5 \approx OCH_2CH_2CH_2CH_3 > OCH(CH_3)_2$, in accord with the observed increase of the hs/ls ratio in the same sequence.

Discussion

Solid-State Magnetism. From the magnetic susceptibility measurements on the solid samples it is clear that the present cobalt(III) complexes can be grouped into two classes. One class contains the complexes **5f** and **5g** with R = alkyl and temperature-independent magnetic moments of ca. 2 μ_B. The alkyl substituents have a rather strong σ-donation tendency and cause a strong ligand field around the central cobalt(III) ion, which therefore adopts a $^1A_1$ (low-spin) ground state over the whole temperature range (see the discussion of the NMR data). The temperature-independent paramagnetism corresponding to ca. 2 μ_B is most probably mainly due to paramagnetic impurities and not to second-order Zeeman effects, which are known to be smaller by a factor of 2–4. The reduction of **5f** and **5g** to give the cobalt(II) compounds **2f** and **2g** is surprisingly fast. This makes the purification of **5f** and **5g** difficult.

The second class comprises the complexes **5a–e**, which apparently exhibit a temperature-induced low-spin $\rightleftharpoons$ high-spin transition at the central cobalt(III) ion, in terms of the ligand field ground states described by $^1A_1(O_h) \rightleftharpoons {}^5T_2(O_h)$ in the approximation of O_h symmetry. There is no indication for an intermediate $S = 1$ state. The same is true for the extensively studied class of iron(II) spin-crossover compounds, which are isoelectronic ($3d^6$) with the cobalt(III) complexes. For the iron complexes it has been well-documented by Mössbauer spectroscopy[3] that the spin-state transition proceeds directly from $S = 0$ to $S = 2$ and vice versa, but never via a detectable $S = 1$ state. This, of course, should have its consequences for the optical transitions, which have in fact been observed simply by the color change from green for the high-spin state at high temperature to yellow for the low-spin state at sufficiently low temperature. The transition behavior is different for each of these spin-crossover complexes as can be seen from the $\mu_{eff}(T)$ curves of Figure 2. At room temperature only a small fraction of the complex molecules of **5a** has been converted to the high-spin state, whereas in **5c** the spin-state conversion to $S = 2$ appears to be complete. In the case of **5b,d,e** the $\mu_{eff}(T)$ curves are still rising in the room-temperature region, indicating that pure high-spin behavior will be reached only far above room temperature. The spin-state conversion is gradual for all complexes, and there has been no indication for the occurrence of a hysteresis in the $\mu_{eff}(T)$ curve; both features are indicative of a non-first-order transition.

The high-spin fraction at a given temperature increases roughly in the order R = $OCH_3 < OC_2H_5 < OCH_2CH_2CH_2CH_3 < OCH_2C(CH_3)_3 < OCH(CH_3)_2$. Similar substituent effects on the spin-crossover behavior are known from studies of the spin transition in iron(III) compounds.[3,22] In general, there are two effects to be considered in the total influence of intraligand substitution on the spin transition behavior, viz. an electronic effect and steric hindrance. The electronic effect refers to changes in the basicity of the coordinating atom (oxygen in the present case) induced by the alkyl substituents, which in turn influence the ligand field strength via changes in the σ-donation power. This electronic effect is considered to be small within the series of complexes **5a–e**. More important is the steric hindrance effect as can be inferred from the crystal structure determination of CoL_2 (**2a**),[25] which has shown that the alkyl substituents from the two ligands approach each other closely. The more bulky the substituents, the more effective will be the steric hindrance, which more and more lengthens the metal–oxygen bond, and this, as is well-known from ligand field theory, weakens the ligand field and favors the high-spin state. This effect dominates here in the order R = $OCH_3 < OC_2H_5 < OCH_2CH_2CH_2CH_3 < OCH_2C(CH_3)_3 < OCH(CH_3)_2$ in the solid samples. But, as will be discussed in more detail in the following, the same steric hindrance effect prevails in solution.

Table II. Equilibrium Constants at 300 K and Thermodynamic Parameters of the Low-Spin to High-Spin Transition in the Cobalt(III) Complexes **5a–d** As Determined from Eq 1

	5a	**5b**	**5c**	**5d**
$\Delta H°$/kJ·mol^{-1}	25.1	24.8	14.1	23.3
$\Delta S°$/J·mol^{-1}·K^{-1}	69	73	56	66
$\Delta G°_{300}$/kJ·mol^{-1}	4.4	2.9	−2.7	3.5
K = hs/ls	0.17	0.31	2.95	0.25
% high spin	15	24	75	20

Spin Equilibrium in Solution: ^{31}P NMR Study. The ^{31}P NMR chemical shifts δ of the cobalt(III) complexes **5a–d,f** as a function of temperature are shown in Figure 3. The observed temperature dependence of δ can be interpreted by fitting eq 1 to the experimental points.

$$\delta = \delta_{ls} + \frac{C}{T(1 + \exp(\Delta G°/RT))} \qquad (1)$$

Equation 1 implies that (a) the hs/ls transition is fast on the NMR time scale, (b) the hs/ls equilibrium constant is given by $\exp(-\Delta G°/RT)$, i.e. a Boltzmann distribution between the high-spin and the low-spin state, (c) the chemical shift of the high-spin species follows a Curie temperature dependence, and (d) the chemical shift of the low-spin species is temperature-independent. From Figure 3 it is evident that eq 1 adequately describes the spin equilibrium in dichloromethane and acetone solution.[23] The thermodynamic parameters of the equilibrium have been obtained by fitting eq 1 to the experimental values $\delta = f(T)$. They are given in Table II. From the data in Tables I and II and Figure 3 it is obvious that the low-spin to high-spin ratio at a given temperature is again strongly dependent on the substituents R. The cobalt(III) complexes **5f,g**, where the substituents R are alkyl groups, are low spin over the whole temperature range. This means that the electron-donating alkyl groups make the ligands **1f,g** stronger than the ligands **1a–e**, where the substituents are electron-withdrawing alkoxy groups. The larger ligand field splitting favors the diamagnetic low-spin configuration. This electronic effect is strong enough to bring the equilibrium completely to the low-spin side. The electron-withdrawing effect of the alkoxy groups should be very similar for all substituents **a–e**. One observes, however, a strong influence of the alkoxy groups on the spin equilibrium constant. From Figure 3 and Table II one can see that the high-spin portion at a given temperature is highest when R is $OCH(CH_3)_2$ and smallest when R is OCH_3.[24] We postulate that this is a consequence of repulsive interligand interaction. From the crystal structure determination of CoL_2 (**2a**)[25] we know that the $OCH_3 \cdots H_3CO$ contact between the two ligands corresponds roughly to the sum of the van der Waals radii. The increasing steric demand of the alkoxy groups will lead to a slight increase in the cobalt–oxygen bond length along the series R = $OCH_3 \lesssim OC_2H_5 \lesssim OCH_2CH_2CH_2CH_3 \ll OCH(CH_3)_2$. The crystal field splitting is, however, highly sensitive to the metal–ligand distance. Depending on whether a monopole or dipole model is used, the expected dependence is $\Delta \approx r^{-5}$ or r^{-6}. Experimental values[26] lie in the range r^{-5} to r^{-8}. This would explain the increase in the hs/ls ratio in the same order R = $OCH_3 \lesssim$

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[22] Martin, R. L.; White, A. H. *Transition Met. Chem.* (*N.Y.*) **1968**, *4*, 113.

[23] For one cobalt(III) complex (**5b**) we have studied the spin equilibrium in different solvents. No significant influence of the solvent has been observed (see ref 10).

[24] If there were a significant difference in the −I effect of the alkoxy groups, one would expect the inverse order.

[25] Dubler, E.; Linowsky, L.; Kläui, W. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 191.

[26] (a) Schläfer, H. L.; Gliemann, G. *Einführung in die Ligandenfeldtheorie*; Akademische Verlagsgesellschaft: Frankfurt am Main, FRG, 1967; Chapter A.I.7.a. (b) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971.

Table III. d–d Transitions and Ligand Field Parameters Δ_0 and B (cm^{-1}) of **2a–d,f** in CH_2Cl_2/CCl_4 and of Comparable Cobalt(II) Compounds[7,27]

	ν_1	ν_2	ν_3	ν_2/ν_1	Δ_0	B	β^c
$[Co(pyNO)_6]^{2+\,a}$	9090		18 980 19 960		10195	766	0.79
$[Co(H_2O)_6]^{2+}$	8100	16 000 17 480^b	19 400	1.975	9200	825	0.85
$[Co(DMSO)_6]^{2+}$	7410	14 600 15 980^b	18 700	1.970	8480	824	0.85
2a	7150	14 600 15 350^b	18 500	2.042	8200	826	0.85
2b	7200	14 700 15 470^b	18 700	2.042	8270	835	0.86
2c	7050	15 600 15 150^b	18 350	2.213	8100	821	0.85
2d	7170	14 500 15 410^b	18 500	2.022	8240	824	0.85
2f	~7200	14 750	...	2.049	...	...	...
$KCoF_3$	7150	15 200 15 420^b	19 200	2.126	8285	877	0.91

[a] pyNO = pyridine *N*-oxide. [b] Calculated from ν_1 and ν_3. [c] B(free ion) = 970 cm^{-1}.

Table IV. d–d Transitions and Ligand Field Parameters Δ_0 and B (cm^{-1}) of **3a–d,f** in CH_2Cl_2/CCl_4 and of Comparable Nickel(II) Compounds[7,27]

	ν_1	ν_2	ν_3	Δ_0	B^c	β^d
$[Ni(pyNO)_6]^{2+\,a}$	8400	14 125	25 840 (?)	8400	984 (?)	0.95 (?)
$[Ni(H_2O)_6]^{2+}$	8500	13 800	25 300	8500	907	0.88
$[Ni(DMSO)_6]^{2+}$	7730	12 970	24 040	7730	921	0.89
3a	7650	13 100	24 300^b	7650	970	0.94
3b	7550	13 000	24 200^b	7550	970	0.94
3c	7100	12 650	23 500^b	7100	990	0.96
3d	7600	13 150	24 200^b	7600	970	0.94
3f	~7600	13 000	~24 200^b	~7600	~960	~0.93
$KNiF_3$	7250	12 530	23 810	7250	973	0.94

[a] pyNO = pyridine *N*-oxide. [b] Calculated, obscured by intraligand absorption. [c] Calculated from $B = (\nu_2 + \nu_3 - 3\nu_1)/15$. [d] B(free ion) = 1030 cm^{-1}.

$OC_2H_5 \lesssim OCH_2CH_2CH_2CH_3 \ll OCH(CH_3)_2$.

Ligand Field Spectroscopic Characterization of the Oxygen Tripod Ligands L⁻ (1a–d,f). In order to confirm our interpretation of the magnetism of the $[CoL_2]^+$ complexes we have measured the electronic spectra of the ML_2 complexes CoL_2 (**2a–d,f**), NiL_2 (**3a–d,f**) and CuL_2 (**4a–d,f**). The electronic spectra of all ML_2 complexes can be analyzed as the sum of the spectra of the ligand chromophore $(C_5H_5)CoP_3$ and of the MO_6 fragment. The intraligand transitions occur in the UV region. The longest wavelength transition lies at $\lambda \approx 340$ nm ($\epsilon \approx 3000$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$ per $(C_5H_5)CoP_3$ unit) in the phosphito complexes (R = alkoxy) and at $\lambda \approx 370$ nm ($\epsilon \approx 2500$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$ per $(C_5H_5)CoP_3$ unit) in the phosphinito complexes (R = alkyl). Its position and intensity are independent of M. The tail of this band absorbs at the blue end of the visible region and causes the yellow color of the ligands L⁻ and their complexes **2**, **3**, and **4**. The d–d transitions, which are observed as weak bands, in the addition to the intraligand absorptions are given in Tables III–V.

In the electronic spectra of octahedral high-spin cobalt(II) complexes one can expect three spin-allowed d–d transitions. The assignment of the transitions $^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1) and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) is unequivocal. The two-electron transition $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) has sometimes been identified as a very weak band near 15 000 cm^{-1} in cobalt(II) complexes with oxygen ligands. Any assignment of a band in this region to ν_2 should, however, be made with extreme caution.[27] We have therefore calculated the ligand field splitting Δ_0 not from the difference $\nu_2 - \nu_1$ but from the transitions ν_1 and ν_3. The intensities of the transitions ν_1 ($\epsilon \approx 1.0$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$), ν_2 ($\epsilon \approx 0.2$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$), and ν_3 ($\epsilon \approx 3.4$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$) are very similar for all complexes **2** and agree with the ones reported for other CoO_6 chromophores like $[Co(H_2O)_6]^{2+}$ (ϵ = 2.0, 0.3, and 4.6 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$). The transition ν_3 in the spectrum of the phosphinito complex **2f** is obscured by the tail of the longest wavelength intraligand absorption. From the frequencies ν_1 and ν_2 one can at least say that the ligand **1f** has ligand field properties very similar to those of **1a–d**.

Table V. d–d Transitions (cm^{-1}) of **4a–d,f** in CH_2Cl_2/CCl_4 and of Comparable Copper(II) Compounds[a]

	E_g	B_{2g}	A_{1g}	Δ_0
$K_2SrCu(NO_2)_6$	16 400		7600	~12 600
$[Cu(H_2O)_6]^{2+}$	12 600	9400		
Sr_2CuWO_6	12 300	9900	8200	~7400
4a	11 300	~8800		
4b	11 200	~8800		
4c	11 000	~8600		
4d	11 200	~8800		
4f	12 050	~8950		
CuF_2	11 400	8850		~6700

[a] See ref 7 and references cited therein.

The ligand field spectra of octahedral nickel(II) complexes consist of three bands, which can be assigned to the three spin-allowed d–d transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}$ (ν_2), and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3). The energy of ν_1 corresponds to the ligand field splitting Δ_0. The intensities of the transitions ν_1 ($\epsilon \approx 1.5$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$) and ν_2 ($\epsilon \approx 1.5$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$) in the ligand field spectra of the NiL_2 complexes **3** are in accord with the low values of the $[Ni(H_2O)_6]^{2+}$ ion (ϵ = 2 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$). ν_3 could not be observed because of the intraligand absorption band mentioned above. The position of ν_3 needed for the evaluation of B was therefore calculated from ν_1 and ν_2.[28]

The ligand field spectra of the copper(II) complexes show an absorption band at 11 000–12 000 cm^{-1} with a distinct shoulder indicating a distorted octahedral coordination geometry. A crystal structure determination of **4b** proves the expected tetragonal elongation of the CuO_6 chromophore.[25] The positions of the

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(27) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968.

(28) This procedure yields not very accurate values of B since the Racah parameter B is only weakly dependent on the frequencies ν_2 and ν_3.

Table VI. $P{=}O$ Stretching Frequencies (cm^{-1}) of $HP(O)R_2$ (Film) and the Oxygen Tripod Compounds **1a–d** (Na Salts), **2a–d**, and **3a–d** (KBr)

R	$HP(O)R_2$	**1**	**2, 3**
OCH_3 (**a**)	1260	1171	1127
OC_2H_5 (**b**)	1258	1170	1130
$OCH(CH_3)_2$ (**c**)	1256	1169	1147
$OCH_2CH_2CH_2CH_3$ (**d**)	1260	1168	1128

absorption bands do not allow the calculation of a value Δ_0, but a direct comparison with the spectra of other six-coordinate copper(II) compounds may be made instead.

The electronic spectra of the cobalt, nickel, and copper complexes ML_2 give a consistent picture of the oxygen tripod ligands L^-. They are all very weak ligands, weaker than most other oxygen ligands. The position of L^- in the spectrochemical series ... $Cl^- < N_3^- < F^- <$ DMS*O* < pyN*O* < $H_2O < CH_3CN < NH_3 \ll NO_2^-$ ... is near that of fluoride. They are also surprisingly hard ligands with a position in the nephelauxetic series $F^- > H_2O >$ DMS*O* > pyN*O* > NH_3 > oxalate(2–) > $Cl^- > N_3^-$ ... near that of dimethyl sulfoxide and water. This characterization of the ligands L^- is in complete agreement with the spin-crossover behavior of the cobalt(III) complexes $[CoL_2]^+$ since, as has been mentioned earlier, $[Co(H_2O)_6]^{3+}$ is a low-spin complex whereas $[CoF_6]^{3-}$ is high spin. The variation of the substituents R in the ligands L^-, which controls the hs/ls ratio along the series $R = OCH(CH_3)_2 \gg OCH_2CH_2CH_2CH_3 \geq OC_2H_5 \geq OCH_3 \gg C_2H_5$, causes, in accord with our hypothesis, a small variation in ligand field strength in the opposite order $R = C_2H_5 > OCH_3 \approx OC_2H_5 \approx OCH_2CH_2CH_2CH_3 > OCH(CH_3)_2$.

Concluding Remarks

Our explanation of the marked influence of the alkoxy substituents on the hs/ls ratio is based on the assumption that there is increasingly more repulsion between the two ligands L^- in ML_2 complexes as the substituents become sterically more demanding. This causes a decrease in ligand field strength because of a slight lenthening of the Co–O bond. Figure 3 and Table II show that the steric effect is most pronounced when $R = OCH(CH_3)_2$. One might suspect that this is not *interligand* repulsion in origin but an *intraligand* effect. The R–P–R angles and/or the P–O–R angles could widen with increasing bulkiness of the substituents R. This would change the relative weight of the s and p orbitals involved in the $P{=}O$ bond with a concomitant change in the donor properties of the ligands. One can, however, distinguish between the two alternative explanations "interligand repulsion" vs "intraligand effect" as follows. The $P{=}O$ stretching vibration gives rise to a strong and isolated band in the infrared spectrum. This band is sensitive to the PO–M interaction. In Table VI are listed the $P{=}O$ stretching frequencies of the secondary phosphites $HP(O)R_2$, the sodium salts of the ligands L^- (**1a–d**), and the 2:1 complexes CoL_2 (**2a–d**) and NiL_2 (**3a–d**). The ML_2 complexes **2** and **3** have a $P{=}O$ stretching frequency that is significantly higher when R is $OCH(CH_3)_2$ than with the smaller substituents R. The higher frequency means weaker PO–M interaction. The sequence $R = OCH_3 \approx OC_2H_5 \approx OCH_2CH_2CH_2CH_3 < OCH(CH_3)_2$ is the same as in the spin equilibrium study (see Figure 3 and Table II). In contrast, the frequencies $\nu(P{=}O)$ of the secondary phosphites $HP(O)R_2$ are in the range 1256–1260 cm^{-1} with no correlation with the steric demand of the groups R. The frequencies $\nu(P{=}O)$ of the sodium salts NaL (**1**) are in the range 1168–1171 cm^{-1}, and again there is no correlation with the bulkiness of R. If the influence of the groups R on the spin equilibrium constant were an intraligand effect and were not due to interligand repulsion, one would expect the same dependence of $\nu(P{=}O)$ in $HP(O)R_2$ and NaL as in the ML_2 complexes.

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Registry No. **1a**·Na, 82149-18-6; **1b**·Na, 70850-86-1; **1c**·Na, 110935-74-5; **1d**·Na, 110935-73-4; **4f**·Na, 87965-88-6; **2a**, 53322-02-4; **2b**, 53322-15-9; **2c**, 83831-09-8; **2d**, 83831-10-1; **2e**, 110935-62-1; **2f**, 87965-84-2; **2g**, 87965-85-3; **3a**, 58438-17-8; **3b**, 58438-23-6; **3c**, 83844-75-1; **3d**, 83844-76-2; **3f**, 110935-63-2; **4a**, 58438-16-7; **4b**, 58438-20-3; **4c**, 110935-64-3; **4d**, 110935-65-4; **4f**, 110935-66-5; **5a**, 83831-11-2; **5b**, 70850-84-9; **5c**, 83831-12-3; **5c**·$SbCl_6$, 110935-70-1; **5d**, 83831-13-4; **5d**·$SbCl_6$, 110935-69-8; **5e**, 110935-60-9; **5e**·$SbCl_6$, 110935-67-6; **5f**, 83844-74-0; **5f**·$SbCl_6$, 110935-72-3; **5f**·PF_6, 110935-71-2; **5g**, 110935-61-0; **5g**·$SbCl_6$, 110935-68-7; $[Co(pyNO)_6]^{2+}$, 47839-54-3; $[Co(H_2O)_6]^{2+}$, 15276-47-8; $[Co(DMSO)_6]^{2+}$, 26745-61-9; $[Ni(pyNO)_6]^{2+}$, 47840-10-8; $[Ni(H_2O)_6]^{2+}$, 15365-79-4; $[Ni(DMSO)_6]^{2+}$, 26745-60-8; $K_2SrCu(NO_2)_6$, 33515-97-8; $[Cu(H_2O)_6]^{2+}$, 14946-74-8; Sr_2CuWO_6, 13827-39-9; $[(p\text{-}BrC_6H_4)_3N]SbCl_6$, 24964-91-8; $[(p\text{-}BrC_6H_4)_3N]PF_6$, 67974-40-7; $KCoF_3$, 13841-81-1; CuF_2, 7789-19-7; $KNiF_3$, 13845-06-2; dineopentyl phosphite, 22289-00-5; 2,2-dimethylpropanol, 75-84-3; dicyclopentadienylcobalt, 1277-43-6; diisopropyl phosphite, 1809-20-7; dibutyl phosphite, 1809-19-4.