reflection for the powdered complexes are also plotted. The intensities for (011) reflections show complicated changes. The relative accuracy of the values is sufficient to establish this result. It is clear that there is no large difference in the structure between high-spin and low-spin states. In addition, the observations are good enough to rule out the possibilities of any crystallographic phase transition associated with a spin transition. The intensity modulation as shown in the figure can be related to the microstructural changes of individual molecules and/or production of clusters of constituent molecules either statically or dynamically. It is, therefore, possible to expect a random distribution of two spin isomers; modulation of the molecular array and the reorderings of the molecular array and/or atomic arrays through the spin transition take place dynamically without a significant domain formation by either of the two spin isomers. In tris(dithiocarbamato)iron(III), which exhibits rapid electronic relaxation, the two spin isomers were not crystallographically resolved and only an average structure was reported.[17]

The mechanism of a continuous spin transition in a solid state and the factors that determine electron-transfer rates are not yet understood although it is pointed out that a coupling between the electronic state and the vibrational modes of a molecule is important for spin transition in solution.[21] In the system studied here, no evidence of first-order transition could be found. It may be important to image a intramolecular mechanism for rapid spin interconversion.

Registry No. Hacpa, 28484-27-7; $[Fe(acpa)_2]PF_6$, 90790-59-3; acetylacetone, 123-54-6; 2-(aminomethyl)pyridine, 3731-51-9.

Supplementary Material Available: Listings of programming data, thermal parameters, and mean-square displacement tensors of atoms (5 pages). Ordering information is given on any current masthead page.

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Structure–NMR Correlations in Halo(ligand)bis(dioximato)cobalt(III) Complexes

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A synthetic scheme leading to chloro(ligand)bis(dimethylglyoximato)- and chloro(ligand)bis(diphenylglyoximato)cobalt(III) complexes in good yields is reported for the cases where the ligand is a nitrogenated aromatic base. Substitution reactions of the axial chloro ligand lead to the cyano ligand derivatives. Single-crystal X-ray diffraction and NMR spectroscopic studies were carried out to characterize the above-mentioned complexes. Crystal structures of the following compounds are reported: $[Co(dmgH)Cl(4\text{-}NCpy)]\cdot{}^1/_3H_2O$ (**1**), $[Co(dmgH)_2X(2,6\text{-}Me_2pz)]$ (X = Cl (**3**) and Br (**13**)), and $[Co(dmgH)_2Cl(3,5\text{-}Me_2pzol)]$ (**5**), where dmgH = dimethylglyoximate(1−), 4-NCpy = 4-cyanopyridine, $2,6\text{-}Me_2pz$ = 2,6-dimethylpyrazine, $2,6\text{-}Cl_2pz$ = 2,6-dichloropyrazine, and $3,5\text{-}Me_2pzol$ = 3,5-dimethylpyrazole. Compound **1** is orthorhombic, space group $P2_12_12_1$, with $Z = 4$ and unit cell parameters $a = 15.690$ (3) Å, $b = 14.367$ (3) Å, and $c = 8.320$ (2) Å. Compound **3** is monoclinic, space group $P2_1/a$, with $Z = 4$ and unit cell parameters $a = 12.827$ (2) Å, $b = 16.836$ (3) Å, $c = 8.667$ (1) Å, and $\beta = 99.10$ (2)°. Compound **5** is monoclinic, space group $P2_1/a$, with $Z = 4$ and unit cell parameters $a = 16.139$ (3) Å, $b = 13.525$ (1) Å, $c = 8.491$ (1) Å, and $\beta = 103.94$ (2)°. Compound **13** is monoclinic, space group $P2_1/a$, with $Z = 4$ and unit cell parameters $a = 13.019$ (2) Å, $b = 16.816$ (3) Å, $c = 8.827$ (1) Å, and $\beta = 98.84$ (2)°. ^1H and ^{13}C NMR chemical shifts of the organic bases show clear correlations with both the position of the atoms relative to the bis(dioximato)cobalt moiety and the wavelength of the Co → dmgH charge-transfer band; these correlations can be rationalized with the aid of the ring-current formalism usually associated with organic aromatic molecules.

The chemistry and molecular structure of bis(dioximato)cobalt(III) complexes (hereafter referred to by the generic name of cobaloximes) have been extensively explored in the last few years[1] due to interest in them as models for important biochemical complexes[2] as well as to their usefulness as catalysts in many chemical processes[3] or as templates in many organic syntheses.[4] In this context, the knowledge of the electronic structure of cobaloximes and the understanding of the related cis and trans influences is sought as a cornerstone for a systematization of the large body of chemical information currently available and for the successful design of novel derivatives with desired properties.

The study of structure–properties relationships might provide a hint toward the understanding of these problems. Several workers[5–7] have investigated ^1H NMR spectra of cobaloximes in order to establish cis and trans influences of X and L ligands in $[Co(dioxH)_2X(L)]$ complexes (dioxH = dioximate(1−) ligand) and found some correlations between the resonance of methylic protons of the $Co(dmgH)_2{}^+$ moiety and the ligand field parameter[6] or the pK_a of the axial L group.[7]

On the other hand, only a few studies on the ^{13}C NMR spectra of cobaloxime derivatives have been previously reported.[5a,8] Attempts to correlate ^1H and ^{13}C resonances were made, but the results were rather poor. A thorough study on ^{31}P NMR spectra and structural data of mixed phosphine–cobaloxime complexes has also been reported.[8,9]

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Pyridine being a popular ligand, a number of structures of mononuclear pyridine–cobaloximes have been determined;[10,11] only a few structures of cobaloximes with other nitrogenated aromatic bases are known.[10,12] On the other hand, bridging of cobaloxime groups with ligands such as pyrazine or 4,4′-bipyridine produces one-dimensional compounds whose electrical properties might be of interest.[13] Between these two classes of compounds there is an uncovered field: the mononuclear compounds with potentially bridging nitrogen donors and related ligands. The lack of sufficient NMR data on this family of compounds has been recently stressed.[1a] Therefore, a systematic study of mononuclear cobaloximes of general formula [Co(dioxH)$_2$X(L)] (X = Cl$^-$, Br$^-$, CN$^-$, H$_2$O, and PPh$_3$; L = 4-NCpy, pz, 2,6-Me$_2$pz, 2,6-Cl$_2$pz, pdz, 4,4′-bpy, and 3,5-Me$_2$pzol (py = pyridine, pz = pyrazine, pdz = pyridazine, bpy = bipyridine, pzol = pyrazole)) was undertaken in order to gain better insight into their spectral and structural properties, in particular (a) the effect of coordination of L to the cobaloxime group on the structure and spectra of L, (b) the influence of the nature of X on the structural and NMR spectral properties of both L (trans influence) and Co(dioxH)$_2^+$ (cis influence) groups (through changes in X, the electronic effects can in principle be varied through a wide range), (c) the influence of L on X and on Co(dioxH)$_2^+$ (L being always an aromatic nitrogen donor, its change offers the possibility of a fine tuning of cis and trans influences), and (d) the conformational properties of L relative to the cobaloxime group.

Experimental Section

3,5-Dimethylpyrazole was prepared according to the method of Willey and Hexner.[14] Dimethylglyoxime and diphenylglyoxime (analytical grade), cobalt(II) chloride (hexahydrate), and other ligands were obtained from standard sources and used as received.

Elemental analyses were carried out at the Instituto de Quimica Bio-Orgânica (CSIC, Barcelona, Spain). Halide analyses were performed with the Schöniger method,[15] and the final determination was made with Volhard's method. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer. ^{1}H and ^{13}C spectra were obtained at 20–25 °C on a Varian XL-200 (200-MHz) spectrometer using CDCl$_3$ (99.8%) as solvent and operating at 200 and 50.28 MHz, respectively; Me$_4$Si was used as an internal standard for the ^{1}H spectra. UV spectra were recorded with a Beckman UV5230 spectrophotometer using CH$_2$Cl$_2$ as solvent.

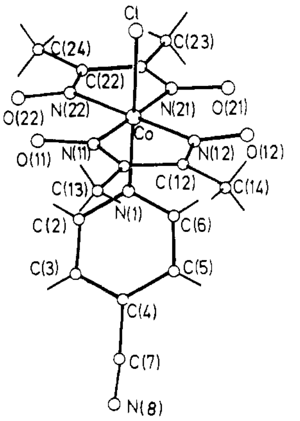

Figure 1. Molecular structure and labeling scheme for compound **1**.

Conductivities of 10^{-3} M acetonic solutions of the new compounds were measured with a Radiometer CDM3 conductivity bridge and found to be smaller than 0.2 Ω^{-1} cm^2 M^{-1} in all cases. Weight losses were found by heating the compounds at 120 °C to constant weight.

Preparation of [Co(dmgH)$_2$Cl(L)] Compounds. The ligand (L = 4-NCpy, pz, 2,6-Me$_2$pz, 2,6-Cl$_2$pz, 3,5-Me$_2$pzol, pdz, 4,4′-bpy; 1 mmol) was added to a solution of [Co(dmgH)$_2$Cl(H$_2$O)][16] (0.36 g, 1 mmol) in acetone (60 mL). The mixture was stirred at room temperature for 30 min. Slow evaporation of the solvent led to crystals or microcrystalline products that were filtered and air-dried. Yields were higher than 60%. For L = 4,4′-bpy, the reaction time was 2 h and the yield poorer (46%).

Preparation of [Co(dpgH)$_2$Cl(L)] Compounds (L = 4-NCpy, pz, 2,6-Me$_2$pz, 2,6-Cl$_2$pz, 3,5-Me$_2$pzol). The procedure described above was used with slight modifications: the amount of solvent (85 mL) and the reaction time (40 min). Yields from 67 to 82% were obtained.

Preparation of [Co(dmgH)$_2$Br(2,6-Me$_2$pz)]. The same procedure as for the chloro derivative was used, but the starting complex was [Co(dmgH)$_2$Br(PPh$_3$)].[16]

Preparation of [Co(dioxH)$_2$(CN)(L)] Compounds (dioxH = dmgH or dpgH; L = 4-NCpy, 2,6-Me$_2$pz). To a solution of [Co(dioxH)$_2$Cl(L)] in acetone was added an equimolar amount of KCN dissolved in water. The mixture was stirred at room temperature for 3 h. The orange precipitate was filtered out, washed with water, and air-dried.

Crystal Structure Determination and Refinement. Brown crystals were obtained by slow evaporation of solutions of the complexes in acetone, to which a few drops of methanol were added. A small crystal (sizes in Table I) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4° < \theta < 9°$) and the cell parameters refined by least squares. Intensities were collected with Mo Kα radiation, with use of the ω-scan technique. The scan speed was 0.03° s^{-1} and the scan width 1.0°. Three intensities were measured every 2 h as orientation and intensity control, and no significant variations were observed. The number of collected reflections and the θ ranges are listed in Table I. Lorentz–polarization corrections and absorption correction were made for compound **13** (maximum and minimum transmission factors for this compound were 0.49 and 0.47, respectively).

The structures were solved by direct methods or Patterson synthesis (Table I), where the positions of the heaviest atoms were located; the positions of the remaining atoms were found from successive weighted Fourier synthesis. The structures were isotropically and anisotropically refined by the full-matrix least-squares method, with use of the SHELX76 computer program;[18] the minimized function was $w = (|F_o| - |F_c|)^2$, where $w = (\sigma(F_o)^2 + k(F_o)^2)^{-1}$ and the values of k are given in Table I. Hydrogen atoms were either located from a difference synthesis or their localization calculated and refined with an isotropic overall temperature coefficient. The occupation factor for the hydrate water oxygen atom in structure **1** was also refined, and the resulting value was 0.33 (1). The final R and R_w values are given in Table I.

Final atomic parameters are listed in Table II, together with their estimated standard deviations. Anisotropic thermal parameters and hydrogen atom coordinates are deposited as supplementary material.

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Table I. Crystal Structure Determination Data

	1	**3**	**5**	**13**
habit	prismatic	prismatic	prismatic	prismatic
cryst size, mm	0.1 × 0.1 × 0.3	0.1 × 0.1 × 0.3	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
measd intens	2889	3851	3288	2863
θ_{max}, deg	30	30	30	30
no. of $I > 2.5\sigma(I)$	2868	3791	3244	2752
determn	Patterson	Patterson	MULTAN	Patterson
refinement	SHELX76	SHELX76	SHELX76	SHELX76
weighting scheme, *k*	0.0168	0.0061	0.0039	0.0
hydrogen	16 (ΔF)	17 (ΔF)	20 (ΔF)	19 (calcd)
final *R*	0.058	0.048	0.037	0.034
R_w	0.068	0.057	0.045	0.040
max shift	−2.38, U_{13} of N(8)	0.86, U_{13} of C(31)	−1.53, U_{13} of C(24)	0.74, *x* of N(4)
max peak in final ΔF	0.4, 0.5 Å from H(2)	0.5, 0.9 Å from C(24)	0.3, 0.7 Å from C(13)	0.3, 0.6 Å from C(12)

Table II. Fractional Atomic Coordinates of Non-Hydrogen Atoms for [Co(dmgH)$_2$Cl(4-NCpy)]·$^1/_3$H$_2$O (**1**), [Co(dmgH)$_2$X(2,6-Me$_2$pz)] (X = Cl (**3**), Br (**13**)), and [Co(dmgH)$_2$Cl(3,5-Me$_2$pzol)] (**5**)[a]

	1			**3**			**13**			**5**		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Co	81245 (3)	94612 (3)	5650 (7)	21248 (3)	19755 (2)	25142 (5)	79016 (3)	19659 (2)	75072 (5)	59124 (2)	26598 (3)	19917 (4)
X	9243 (1)	10164 (1)	−586 (2)	36648 (7)	24977 (6)	25877 (12)	63190 (3)	25213 (2)	63881 (6)	66700 (4)	19793 (6)	3766 (10)
O(11)	7837 (4)	11087 (3)	2448 (6)	1534 (2)	3459 (2)	1059 (3)	8498 (2)	3461 (1)	8939 (3)	5751 (1)	4446 (2)	179 (3)
N(11)	8227 (3)	10260 (3)	2374 (5)	1544 (2)	3011 (2)	2349 (3)	8474 (2)	3003 (1)	7632 (4)	6231 (1)	3933 (2)	1405 (3)
C(11)	8720 (4)	9972 (5)	3535 (6)	1181 (3)	3282 (2)	3554 (4)	8828 (2)	3273 (2)	6500 (4)	6932 (2)	4303 (2)	2292 (4)
C(12)	9111 (3)	9076 (4)	3191 (6)	1265 (3)	2705 (2)	4837 (4)	8734 (2)	2706 (2)	5232 (4)	7380 (2)	3604 (2)	3540 (4)
N(12)	8888 (3)	8736 (3)	1804 (5)	1694 (3)	2039 (2)	4496 (4)	8319 (2)	2041 (1)	5536 (3)	6955 (1)	2802 (2)	3581 (3)
O(12)	9192 (3)	7919 (3)	1278 (7)	1848 (3)	1444 (2)	5538 (3)	8166 (2)	1443 (2)	4499 (3)	7309 (1)	2062 (2)	4580 (3)
C(13)	8881 (6)	10552 (7)	5002 (8)	728 (4)	4088 (3)	3677 (6)	9265 (3)	4103 (2)	6355 (6)	7225 (2)	5331 (3)	2064 (6)
C(14)	9688 (6)	8592 (8)	4356 (11)	928 (5)	2879 (3)	6369 (5)	9030 (4)	2882 (3)	3641 (5)	8251 (2)	3766 (3)	4580 (5)
O(21)	7067 (3)	11024 (2)	−143 (6)	3586 (2)	2572 (2)	−368 (3)	7452 (2)	2577 (1)	10371 (3)	6141 (2)	837 (2)	3700 (3)
N(21)	7365 (2)	10192 (3)	−666 (5)	2646 (2)	1947 (2)	6597 (4)	7394 (2)	1952 (2)	9436 (3)	5622 (2)	1374 (2)	2553 (3)
C(21)	7110 (3)	9847 (4)	−2036 (6)	3133 (3)	1307 (3)	299 (5)	6886 (2)	1295 (2)	9750 (5)	4911 (2)	1025 (2)	1719 (4)
C(22)	7519 (3)	8935 (4)	−2372 (6)	3136 (3)	703 (2)	1511 (5)	6887 (2)	690 (2)	8492 (5)	4461 (2)	1698 (2)	458 (4)
N(22)	8038 (3)	8675 (3)	−1256 (5)	2716 (2)	947 (2)	2690 (4)	7295 (2)	940 (2)	7328 (4)	4891 (1)	2498 (2)	365 (3)
O(22)	8477 (3)	7866 (3)	−1386 (6)	2658 (3)	475 (2)	3928 (4)	7355 (2)	467 (1)	6072 (4)	4585 (1)	3212 (2)	−724 (3)
C(23)	6481 (6)	10339 (8)	−3109 (12)	3704 (5)	1232 (5)	−1084 (7)	6372 (3)	1240 (3)	11156 (6)	4618 (3)	−7 (3)	2008 (7)
C(24)	7361 (6)	8397 (7)	−3893 (7)	3584 (3)	−113 (3)	1420 (8)	6418 (3)	−125 (2)	8597 (6)	3598 (3)	1497 (4)	−605 (6)
N(1)	7145 (3)	8821 (3)	1546 (5)	776 (2)	1494 (2)	1559 (3)	9222 (2)	1491 (1)	8423 (3)	5213 (1)	3294 (2)	3323 (3)
N(2)										4604 (2)	3960 (2)	2609 (3)
C(2)	7105 (3)	7888 (3)	1521 (6)	217 (3)	1047 (2)	2399 (5)	9768 (2)	1024 (2)	7604 (4)			
C(3)	6404 (4)	7405 (3)	2051 (8)	693 (3)	676 (2)	1741 (5)	10667 (2)	645 (2)	8255 (4)	4113 (2)	4244 (2)	3601 (4)
C(4)	5709 (3)	7911 (4)	2655 (6)							4424 (2)	3764 (3)	5035 (4)
N(4)				1042 (3)	721 (2)	207 (4)	11063 (2)	710 (2)	9784 (4)			
C(5)	5758 (3)	8875 (4)	2722 (7)	484 (3)	1184 (2)	−631 (5)	10524 (2)	1196 (2)	10631 (5)	4424 (2)	3764 (3)	5035 (4)
C(6)	6470 (3)	9308 (3)	2147 (7)	393 (3)	1575 (2)	47 (4)	9609 (2)	1585 (2)	9905 (4)	3383 (2)	4939 (3)	3091 (6)
C(7)	4947 (4)	7400 (5)	3178 (7)	1345 (3)	214 (3)	2729 (8)	11301 (3)	163 (3)	7348 (6)	5627 (3)	2499 (4)	6051 (5)
N(8)	4371 (4)	6988 (6)	3541 (9)									
C(8)				905 (4)	1267 (4)	−2350 (6)	10967 (3)	1288 (3)	12320 (5)			
OW	4009 (8)	3623 (10)	8680 (17)									

[a] Estimated standard deviations are in parentheses. Coordinates are $\times 10^4$ except those for Co and X ($\times 10^5$).

Table III. Electronic and NMR Spectral Data for the New Compounds

		^{1}H NMR		^{13}C NMR	
compd	λ_{max}, nm[a]	δ(dioxH)	δ(L)	δ(dioxH)	δ(L)
[Co(dmgH)$_2$Cl(4-NCpy)] (**1**)	242 (sh) L 271 (4.72) MLCT	2.41	7.48 dd (H$_\alpha$) 8.53 dd (H$_\beta$)	13.22 (CH$_3$) 152.7 (C=N)	118.03 (CN) 127.70 (C$_\beta$) 152.07 (C$_\alpha$)
[Co(dmgH)$_2$Cl(pz)] (**2**)	235 (4.54) L 261 (4.57) MLCT	2.42	8.32 dd (H$_\alpha$) 8.52 dd (H$_\beta$)		
[Co(dmgH)$_2$Cl(2,6-Me$_2$pz)] (**3**)	233 (sh) L 274 (4.29) MLCT	2.42	2.48 (CH$_3$) 7.94 (H$_\alpha$)	13.11 (CH$_3$) 155.56 (C=N)	21.12 (CH$_3$) 141.20 (C$_\alpha$) 152.75 (C$_\beta$)
[Co(dmgH)$_2$Cl(2,6-Cl$_2$pz)] (**4**)	275 (4.67) MLCT + L				
[Co(dmgH)$_2$Cl(3,4-Me$_2$pzol)] (**5**)	236 (sh) L 259 (4.47) MLCT	2.48	2.09 (3-CH$_3$) 2.21 (5-CH$_3$) 5.59 (4-H)	13.07 (CH$_3$) 157.00 (C=N)	11.4 (3-CH$_3$) 12.98 (5-CH$_3$) 108.57 (3-C) 108.70 (5-C) 143.25 (4-C)
[Co(dmgH)$_2$Cl(pdz)] (**6**)	266 (4.58) MLCT	2.40	7.53 t (4-C, 5-C) 9.04 m (3-C, 6-C)		
[Co(dmgH)$_2$Cl(4,4′-bpy)] (**7**)	256 (4.38) MLCT				
[Co(dpgH)$_2$Cl(4-NCpy)] (**8**)	234 (4.44) L 267 (4.33) MLCT	7.36 m (Ph)	7.60 dd (H$_\alpha$) 8.81 dd (H$_\beta$)	154.05 (C=N)	114.7 (C$_\gamma$) 119.91 (CN) 127.17 (C$_\beta$) 152.07 (C$_\alpha$)
[Co(dpgH)$_2$Cl(pz)] (**9**)	230 (sh) L 264 (4.28) MLCT				
[Co(dpgH)$_2$Cl(2,6-Me$_2$pz)] (**10**)	245 (sh) 275 (4.60) MLCT	7.25 m (Ph)	2.56 (CH$_3$) 8.30 (H$_\alpha$)	156.18 (C=N)	22.09 (CH$_3$) 141.30 (C$_\alpha$) 153.10 (C$_\beta$)
[Co(dpgH)$_2$Cl(2,6-Cl$_2$pz)] (**11**)	236 (4.58) 265 (4.66) MLCT	7.25 m (Ph)	8.68 (H$_\alpha$)		
[Co(dpgH)$_2$Cl(3,5-Me$_2$pzol)] (**12**)	232 (4.58) L 266 (4.63) MLCT	7.20 m (Ph) 7.29 m (Ph)	2.17 (3-CH$_3$) 2.37 (5-CH$_3$) 5.79 (4-H)	154.04 (C=N)	10.94 (3-CH$_3$) 13.14 (5-CH$_3$) 109.17 (3-C, 5-C) 143.74 (4-C)
[Co(dmgH)$_2$Br(2,6-Me$_2$pz)] (**13**)	230 (4.56) 270 (4.12) MLCT	2.42 (CH$_3$)	2.48 (CH$_3$) 8.03 (H$_\alpha$)		
[Co(dmgH)$_2$CN(4-NCpy)] (**14**)	242 (4.32) L 267 (4.66) MLCT	2.26 (CH$_3$)			
[Co(dmgH)$_2$CN(2,6-Me$_2$pz)] (**15**)	245 (4.48) L 280 (sh) MLCT	2.27 (CH$_3$)	2.56 (CH$_3$) 8.09 (H$_\alpha$)	12.79 (CH$_3$)	22.02 (CH$_3$) 139.81 (C$_\alpha$) 152.51 (C$_\beta$)
[Co(dpgH)$_2$CN(2,6-Me$_2$pz)] (**16**)	258 (4.41)				

[a] MLCT = metal to ligand charge-transfer band. log ϵ is given in parentheses.

Crystal Data. $C_{14}H_{18}ClCoN_6O_4\cdot{}^1/_3H_2O$ (**1**): $M_r = 434.73$, orthorhombic, $a = 15.690$ (3) Å, $b = 14.367$ (3) Å, $c = 8.320$ (2) Å, $U = 1875$ (1) Å^3, $Z = 4$, $D_{calcd} = 1.54$ g cm^{-3}, $F(000) = 893.3$, μ(Mo Kα) = 11.3 cm^{-1}, $T = 298$ K, space group $P2_12_12_1$.

$C_{14}H_{22}ClCoN_6O_4$ (**3**): $M_r = 432.7$, monoclinic, $a = 12.827$ (2) Å, $b = 16.836$ (3) Å, $c = 8.667$ (1) Å, $\beta = 99.10$ (2)°, $Z = 4$, $D_{calcd} = 1.55$ g cm^{-3}, $F(000) = 896$, μ(Mo Kα) = 11.4 cm^{-1}, $T = 294$ K, space group $P2_1/a$.

$C_{13}H_{22}ClCoN_6O_4$ (**5**): $M_r = 420.74$, monoclinic, $a = 16.139$ (3) Å, $b = 13.525$ (1) Å, $c = 8.491$ (1) Å, $\beta = 103.94$ (2)°, $Z = 4$, $D_{calcd} = 1.55$ g cm^{-3}, $F(000) = 868$, μ(Mo Kα) = 11.7 cm^{-1}, $T = 294$ K, space group $P2_1/a$.

$C_{14}H_{22}BrCoN_6O_4$ (**13**): $M_r = 478.2$, monoclinic, $a = 13.019$ (2) Å, $b = 16.816$ (3) Å, $c = 8.827$ (1) Å, $\beta = 98.84$ (2)°, $Z = 4$, $D_{calcd} = 1.66$ g cm^{-3}, $F(000) = 972$, μ(Mo Kα) = 31.8 cm^{-1}, $T = 294$ K, space group $P2_1/a$.

Results and Discussion

Synthesis and Reactivity. Addition of nitrogen donor ligands L such as 4-cyanopyridine, pyrazine, 2,6-dimethylpyrazine, 2,6-dichloropyrazine, pyridazine, 4,4′-bipyridine, and 3,5-dimethylpyrazole to solutions of [Co(dioxH)$_2$Cl(H$_2$O)], where dioxH represents dimethyl- or diphenylglyoximate(1−), results in the substitution of the axial H$_2$O group by the organic ligand. In the studied cases, the reactions lead to pure chloro ligand complexes in good yields (typically 70%). The compounds were characterized by their elemental analyses (supplementary material) and infrared, UV, and NMR (^{1}H and ^{13}C) spectra; spectral information is presented in Table III.

In order to obtain the cyano ligand derivatives, the method described by Sasaki and Matsunaga was tried.[19] The product obtained, however, was a mixture of the cyano complex, a double complex salt, and μ-cyano derivatives. These results are in agreement with those reported by Marzilli et al.[20] To avoid these problems, the substitution of the axial chloro ligand by the CN$^-$ group in [Co(dioxH)$_2$Cl(L)] was carried out by adding KCN to a solution of the complex in a 1:1 molar ratio, giving pure cyano ligand complexes in good yields. If the CN$^-$/complex molar ratio is increased, it is possible to replace both axial ligands by the cyano group, leading to the anionic [Co(dioxH)$_2$(CN)$_2$]$^-$ complexes.[21]

Description of the Structures. A perspective drawing of the molecular structure of compound **1** and the numbering scheme are presented in Figure 1. The molecular structure of compound **3** is shown in Figure 2, together with the numbering scheme for

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Table IV. Bond Distances and Angles with Estimated Standard Deviations in Parentheses[a]

Bond Distances (Å)

	1	3	5	13	lit.
Co–X	2.233 (1)	2.228 (1)	2.241 (1)	2.3382 (3)	2.25 (2) (X = Cl)
Co–N(1)	1.963 (4)	1.970 (3)	1.977 (2)	1.954 (2)	
Co–N(11)	1.897 (4)	1.896 (3)	1.897 (2)	1.893 (2)	1.897 (2)
Co–N(12)	1.889 (4)	1.889 (3)	1.894 (2)	1.905 (3)	
Co–N(21)	1.886 (4)	1.887 (3)	1.892 (2)	1.919 (3)	
Co–N(22)	1.892 (4)	1.890 (3)	1.893 (2)	1.893 (3)	
C(11)–N(11)	1.303 (7)	1.292 (5)	1.298 (3)	1.248 (5)	1.296 (2)
C(12)–N(12)	1.300 (6)	1.305 (5)	1.289 (3)	1.288 (4)	
C(21)–N(21)	1.304 (6)	1.293 (5)	1.284 (4)	1.337 (4)	
C(22)–N(22)	1.288 (6)	1.295 (6)	1.297 (4)	1.297 (5)	
C(11)–C(12)	1.450 (8)	1.468 (5)	1.473 (4)	1.461 (5)	1.466 (3)
C(21)–C(22)	1.481 (8)	1.463 (6)	1.459 (5)	1.507 (6)	
C(11)–C(13)	1.498 (8)	1.487 (5)	1.497 (4)	1.521 (4)	1.498 (2)
C(12)–C(14)	1.495 (8)	1.489 (6)	1.486 (4)	1.541 (6)	
C(21)–C(23)	1.503 (8)	1.506 (7)	1.513 (5)	1.500 (6)	
C(22)–C(24)	1.501 (8)	1.498 (6)	1.492 (5)	1.508 (5)	
N(11)–O(11)	1.334 (5)	1.347 (4)	1.333 (3)	1.384 (4)	1.345 (2)
N(12)–O(12)	1.337 (5)	1.344 (3)	1.346 (3)	1.354 (3)	
N(21)–O(21)	1.352 (5)	1.339 (4)	1.336 (3)	1.331 (4)	
N(22)–O(22)	1.351 (5)	1.347 (5)	1.345 (3)	1.377 (4)	
O(11)---O(22)	2.473 (7)	2.472 (4)	2.579 (3)	2.488 (4)	2.497 (4)
O(12)---O(21)	2.485 (7)	2.479 (4)	2.630 (3)	2.487 (4)	

Bond Angles (deg)

	1	3	5	13	lit.
N(11)–Co–X	90.1 (1)	88.8 (1)	89.5 (1)	88.3 (1)	
N(12)–Co–X	89.2 (1)	88.0 (1)	87.6 (1)	86.8 (1)	
N(21)–Co–X	90.6 (1)	87.9 (1)	89.0 (1)	88.8 (1)	
N(22)–Co–X	88.9 (1)	90.6 (1)	90.8 (1)	90.0 (1)	
N(11)–Co–N(1)	91.1 (1)	92.2 (1)	89.1 (1)	92.3 (1)	
N(12)–Co–N(1)	90.6 (1)	92.4 (1)	94.6 (1)	92.8 (1)	
N(21)–Co–N(1)	89.5 (1)	91.7 (1)	92.5 (1)	91.7 (1)	
N(22)–Co–N(1)	89.8 (1)	88.3 (1)	87.1 (1)	89.1 (1)	
N(11)–Co–N(12)	81.1 (2)	81.3 (1)	81.1 (1)	80.0 (1)	81.4 (1)
N(21)–Co–N(22)	81.4 (2)	81.6 (1)	81.4 (1)	82.3 (1)	
Co–N(11)–C(11)	116.4 (3)	116.9 (2)	116.8 (2)	118.6 (2)	116.4 (1)
Co–N(12)–C(12)	116.5 (3)	116.7 (2)	116.9 (2)	115.8 (2)	
Co–N(21)–C(21)	117.1 (3)	116.5 (3)	116.3 (2)	116.3 (3)	
Co–N(22)–C(22)	116.6 (3)	116.0 (3)	115.9 (2)	116.5 (3)	
N(11)–C(11)–C(12)	112.6 (6)	112.7 (3)	112.2 (2)	112.3 (3)	112.8 (1)
N(12)–C(12)–C(11)	113.2 (6)	112.4 (3)	112.8 (2)	113.3 (3)	
N(21)–C(21)–C(22)	111.5 (6)	112.6 (4)	113.3 (3)	110.4 (3)	
N(22)–C(22)–C(21)	115.6 (6)	113.1 (3)	112.7 (2)	114.3 (3)	
Co–N(11)–O(11)	122.3 (3)	122.0 (2)	122.3 (2)	121.3 (2)	122.6 (1)
Co–N(12)–O(12)	122.0 (3)	122.3 (3)	122.8 (2)	122.3 (2)	
Co–N(21)–O(21)	122.2 (3)	122.4 (2)	122.1 (2)	123.1 (2)	
Co–N(22)–O(22)	122.6 (3)	122.3 (3)	122.0 (2)	121.3 (3)	

[a] Literature values are the averages for a large number of nonorganometallic cobaloximes reported in ref 1a.

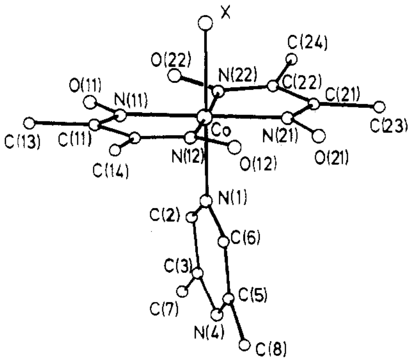


Figure 2. Molecular structure and labeling scheme for compounds **3** (X = Cl) and **13** (X = Br).

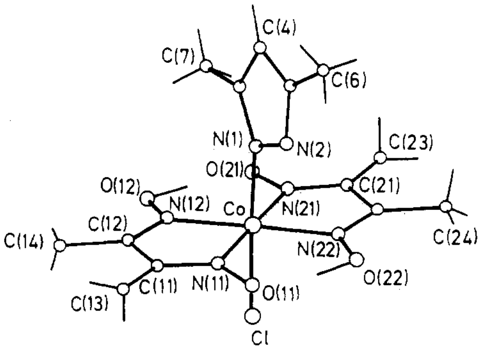


Figure 3. Molecular structure and labeling scheme for compound **5**.

compounds **3** (X = Cl) and **13** (X = Br). A perspective drawing of the molecular structure of compound **5** is presented in Figure 3. In all cases, the structure consists of discrete molecules linked by van der Waals forces. The water molecules in **1** occupy an interstitial site with intermolecular distances larger than the standard values observed for hydrogen bonds. The Co atom is linked to four nitrogen atoms belonging to two dimethylglyoximato ligands in an equatorial plane, the deviations from the mean CoN_4 plane being smaller than 0.041 Å for all the compounds, similar to those found for analogous compounds except for those with bulky axial ligands, where displacements of up to 0.17 Å are observed.[1a] Cl or Br and the N of the organic base occupy the axial positions, thus completing the octahedral coordination sphere of the Co atom. Both the Co–X and the Co–N(axial) bonds are practically perpendicular to the cobaloxime plane, as seen in the N(eq)–Co–X and N(eq)–Co–N(ax) bond angles (Table IV).

The Co–N(dmgH) bond distance has a mean value for the reported structures of 1.895 (8) Å, similar to the average 1.897 (2) Å observed for a large number of nonorganometallic cobaloximes.[1a] Other bond distances in the (dimethylglyoximato)cobalt(III) fragment (Table IV) fall well within the range of experimental values for analogous compounds with different axial ligands. Also, the bond angles fall within the expected range.

The Co–N(axial) bond distances show only slight variations from one ligand to another (1.94–1.98 Å), despite the differences between the ligands. This distance compares well with those found in pyridine–cobaloximes[10,11] (1.97–2.09 Å). For the case of 2,6-Me_2pz (compounds **3** and **13**), that distance is clearly shorter than in a *catena*-(μ-pyrazine)bis(dimethylglyoximato)cobalt(II) compound (2.242 Å).[13a] The Co-Cl bond distances, 2.228–2.253 Å, agree well with those found in chloro(amine)cobaloximes,[12g,22] with an average value of 2.246 (15) Å, significantly shorter than for chloro(phosphine)cobaloximes (average 2.288 (9) Å for six compounds[1a]) or a chloro(alkyl)cobaloxime (2.382 Å).[23]

All the organic ligands are planar. For compound **1**, the geometry of that ligand is not significantly different from that of the free ligand.[24] The geometry of 3,5-Me_2pzol in compound **5** is also similar to that reported in a different cobalt complex.[25] On the other hand, bond distances in 2,6-Me_2pz (Table V) are only slightly different from those in a related pyrazine-bridged cobalt(II) compound.[13a] Slight variations in bond distances when the trans ligand is changed suggest an expansion of the pyrazine ring: the perimeter of 8.072 Å for the chloro derivative changes to 8.224 Å for the bromo derivative, the most significant changes corresponding to bond distances (N(4)–C(3) and N(4)–C(5). This result could be attributed to the electronic trans influence of the halo ligand.

Table V. Bond Distances and Angles for the 2,6-Me_2pz Ligand with Cl (Compound 3) and Br (Compound 13) in a Trans Position

Bond Distances (Å)

	3	13
Co–N(1)	1.970 (3)	1.954 (2)
N(1)–C(2)	1.333 (4)	1.343 (4)
N(1)–C(6)	1.331 (4)	1.338 (4)
N(4)–C(3)	1.336 (5)	1.373 (4)
N(4)–C(5)	1.339 (5)	1.378 (4)
C(2)–C(3)	1.368 (5)	1.379 (4)
C(5)–C(6)	1.365 (5)	1.413 (4)
C(3)–C(7)	1.505 (6)	1.477 (5)
C(5)–C(8)	1.506 (6)	1.525 (5)

Bond Angles (deg)

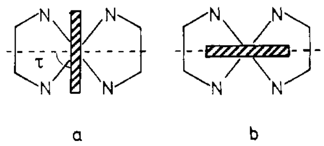
	3	13
C(2)–N(1)–C(6)	116.6 (3)	116.4 (2)
C(3)–N(4)–C(5)	116.8 (3)	115.7 (2)
N(1)–C(6)–C(5)	121.8 (4)	123.4 (3)
N(1)–C(2)–C(3)	121.9 (3)	122.1 (3)
N(4)–C(3)–C(2)	121.2 (4)	122.6 (3)
N(4)–C(5)–C(6)	121.5 (4)	119.6 (3)

Table VI. Conformational Orientation[a] of the Planar Axial Ligand in Cobaloximes of the Type [Co$(dmgH)_2$X(L)]

X[b]	L[b]	τ, deg	ref
Cl	4-NCpy	88.6	this work (**1**)
L^6	4-NCpy	87.5	12c
NCEt	4-NCpy	88.6	12d
		86.6	
		89.0	
L^8	4-Cl(py)	84.6	12e
Cl	2,6-Me_2pz	68.9	this work (**3**)
Br	2,6-Me_2pz	70.0	this work (**13**)
Cl	3,5-Me_2pzol	85.5	this work (**5**)
L^1	py	85.3	11c
CH_3	py	89.7	10a
CH_3NO_2	py	89.6	10b
N_3^-	py	82.2	11b
N_3^-	py	89.5	11h
DDT	py	80.2	11a
$OOCH_2Ph$	py	88.5	11d
L^2	py	87.8	11e
L^3	py	90.0	11e
L^4	py	89.5	11f
$(CN)_4Et$	py	84.1	11g
L^5	py	86.6	11m
L^7	py	87.7	11i
PPh_3	L^9	70.5	12f
pcp	Im	45.5	12b
CH_3	*N*-MeIm	22.0	10a
OH	*N*-MeIm	22.8	10a

[a] Values of τ (**17**) correspond to the average of two crystallographically nonequivalent angles; these two values are in general not significantly different. All conformational angles have been calculated by the authors from published crystallographic coordinates. [b] Legend: Im = imidazole; pcp = 1,3,4,5-tetracyano-2-pentylcyclopentyl; L^1 = ((*p*-methylphenyl)ethoxy)dioxy; L^2 = $CH_2C(CH_3)_3$; L^3 = $CH_2Si(CH_3)_3$: L^4 = $C(CH_3)_2$; L^5 = $CH_2C(CH_3)(CO_2C_2H_5)_2$; L^6 = 2,2,2-trifluoroethyl; L^7 = (1-methoxycaboxy)methyl; L^8 = (1-methoxycarboxy)ethyl; L^9 = 5-(trifluoromethyl)tetrazole.

The planar organic bases are practically perpendicular to the cobaloxime plane, showing a marked conformational preference. The most symmetric orientations of the axial ring correspond to τ = 0° and τ = 90° (for the definition of τ see **17**); a value of $\tau \simeq 40°$ would correspond to an eclipsed conformation of the ring relative to the N(11)–Co–N(21) or N(12)–Co–N(22) axes. All the studied compounds show rotation angles τ larger than 40° (Table VI); i.e., the conformation is closer to **17a** than to **17b** (τ = 0°). That this is a general trend in the family of compounds under study can be seen from the data displayed in Table VI, calculated from the crystallographic coordinates in the literature. This finding is in clear contrast to what is found for a related cobalt(III) derivative of disalicylidene-*o*-phenylenediamine,[27a] where τ < 40°. The exceptions to this rule correspond to those cases in which the axial ligand is imidazole or its *N*-methyl derivative,[10a,12b] suggesting that the conformational preference is of electronic nature. It is noteworthy that in imidazole derivatives of metalloporphyrins no preferred conformation is found.[27b]



17

Spectra. The ^{1}H NMR spectra of the dimethylglyoximate derivatives show a single signal between 2.20 and 2.40 ppm while the diphenylglyoximate analogues present a multiplet between 7.20 and 7.30 ppm (Table III). Those signals are due to the methylic and phenylic protons of the dioximate group, respectively. In general, only one signal is observed for the four equatorial groups, indicating rapid rotation around the Co–N bond. Although two signals can be assigned to the phenylic groups of dpgH in the 3,5-Me_2pzol derivative (**12**), they cannot be attributed to nonequivalent phenyl groups but to the two major components of the phenylic multiplet. Other dpgH compounds present only one signal

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in that region because the other component is masked by the resonance of the solvent (7.24 ppm), and two lines can indeed be observed if the spectrum is measured in CD_2Cl_2, or a second-order multiplet if the spectrum is obtained under higher resolution conditions.

The resonance of the axial ligand protons in $[Co(dmgH)_2X(L)]$ are shifted upfield upon coordination, in agreement with similar studies[28] but in a direction opposite to that expected for an inductive effect involving donation from the ligand to the metal; furthermore, a poor correlation is found between those shifts and the pK_a of the axial ligand, clearly indicating that the inductive effect either is not the main factor acting upon the studied nuclei or is approximately constant for the family of ligands being considered. Apparently, a different situation appears for the analogous compounds with dpgH, where the axial ligand signals are not very sensitive to coordination. This difference can be easily explained by taking into account the presence of phenylic rings in the neighborhood of the axial ligand, producing deshielding of its nuclei. In effect, the values of the shielding constants determined according to Johnson andd Bovey[29] indicate that the presence of the phenylic groups should produce a shift of $\simeq$+0.2 ppm on the signals of the α-protons of the axial ligand. It can be concluded that the same effect operates for both dmgH and dpgH, producing an upfield shift on the axial ligand signals, and this effect is compensated in the case of dpgH by the long-range effect of the phenyl substituents of the equatorial ligand.

The upfield shift of the ^1H NMR signals of the axial ligands upon coordination can be explained in terms of a ring-current effect due to the electronic delocalization throughout the $Co(dioxH)_2^+$ moiety.[30] Several facts support this explanation: (a) a good correlation between the coordination shift $\Delta\delta_L$ (eq 1)[30] and the position of the ligand protons relative to the $Co(dioxH)_2^+$ group;

$$\Delta\delta_L = \delta_L(\text{complex}) - \delta_L(\text{free ligand}) \qquad (1)$$

(b) a good correlation between the coordination shift $\Delta\delta_L$ of the axial ligand and the chemical shift of the cobaloxime methyl group (for dioxH = dmgH) for three families of cobaloximes; (c) a good correlation between the coordination shift of the axial ligand and the Co → dmgH charge-transfer band.

A similar correlation between chemical shifts of the equatorial methyl groups and those of the H_α atoms of the *t*-Bu(py) ligand in a series of $rCo(dmgH)_2X(t\text{-Bu(py)})]$ compounds has been previously reported and interpreted in terms of the magnetic anisotropy of the cobalt atom.[5c] When considering the equatorial methyl groups, however, one would expect the magnetic anisotropy from the closer C=N double bonds to be more important than that from the cobalt atom. The fact that the chemical shifts of the axial protons, affected by the cobalt electrons, are correlated with those of the equatorial methyls, affected by the C=N bonds, indicates electronic delocalization throughout the CoN_4C_4 system. Slight but significative variations in the structure of dimethylglyoxime upon coordination[1a] support the existence of such electronic delocalization. Therefore, it seems appropriate to explain the chemical shifts in terms of the magnetic anisotropy of the whole $Co(dmgH)_2^+$ metallabicycle (i.e., ring-current effect) rather than consider separate effects for the Co atom and the C=N bonds.

It must be noticed that in the studied compounds the axial ligands are themselves aromatic and coordination might result in changes in their "ring-current" intensity. This would also have effects on the axial ligand protons opposite of those on the equatorial protons. This explanation seems unlikely, however, if one recalls the much larger effect of the trans ligand on the chemical shift of the α-protons than on the chemical shift of the β-protons.[13c]

The upfield coordination shifts of the H_α atoms of the axial ligand, as well as the downfield shifts of the cobaloxime methylic protons, are found to follow the trends in eq 2–4.

$$2,6\text{-}Me_2pz > 4\text{-}NCpy > pdz > pz > 3,5\text{-}Me_2pzol \qquad (2)$$

$$Cl^- \simeq H_2O > Br^- > PPh_3 >> CN^- \qquad (3)$$

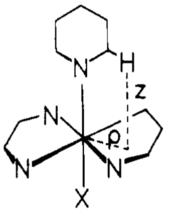
$$dmgH > dpgH \qquad (4)$$

The ligand ordering in eq 2 is the same as that of their Co → dmgH charge-transfer wavelengths. This holds true also for eq 3 (see the wavelengths for L = 2,6-Me_2pz, X = Cl, Br, CN in Table III). Does that mean the NMR coordination shifts and the changes in Co → dmgH charge-transfer wavelength for a differnt axial ligand have a common origin? Actually, a good correlation between both parameters has been found for the α-protons of the axial ligands.

A general picture of the trends discussed so far in ^1H NMR spectra of the axial ligands is provided by the multilinear relationship in eq 5 (multilinear regression coefficient 0.988, standard error of estimate 0.03 ppm), where ρ and z are the cylindrical

$$\Delta\delta_L(^1H) = 2.211 + 0.118\rho + 0.078z - 0.011\lambda \qquad (5)$$

coordinates of a particular proton (in Å), defined as in **18**, and



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λ is the wavelength of the Co → dmgH charge-transfer band (in nm). The α- and β-protons and methylic protons (average position) of compounds **1**, **3**, **5**, and **13** were included in the regression. The independent term in eq 5 probably reflects an inductive effect, which would produce a downfield coordination shift. The three remaining terms might reflect the effect of the "ring current" of the cobaloxime group: for small values of ρ and z (i.e., protons close to the equatorial plane), the coordination shift becomes negative (upfield shift), whereas for large ρ and z values the negative term is compensated, as should be expected for a ring-current effect.

The correlation between $\Delta\delta_L$ and λ(Co → dmgH) has not been previously studied, but its meaning seems clear: the changes introduced in the electronic structure of the $Co(dmgH)_2^+$ group by changes in the axial ligand X (cis influence) are related to the changes produced in the shielding of the nuclei of the axial ligand L (trans influence). Why are these two effects related? Let us assume the existence of a certain degree of π-electron delocalization throughout the $Co(dmgH)_2^+$ group; this delocalization is evident in small but significative changes in bond distances from the free ligand in its neutral ($dmgH_2$) and dianionic (dmg^{2-}) forms, to the complexed $dmgH^-$.[1a] Changing the axial ligands produces different degrees of back-bonding interactions, which can be better understood with the aid of **19**, a schematic orbital diagram for the interaction between the equatorial group $Co(dmgH)_2^+$ and the axial ligands X and L (all the subsequent discussion based on diagram **19** is supported by molecular orbital calculations of the extended-Hückel type): A strong back-bonding interaction (**19a**) between the "d_{xz}" orbital (which is actually mixed with a π orbital of the dioximato ligand) and empty π^* orbitals of the axial ligands produces (a) an important decrease of the energy of d_{xz}, hence a decrease of the charge-transfer band wavelength, and (b) an important mixing of the π^*_L orbital into "d_{xz}", i.e., a partial depopulation of the delocalized π-system of the equatorial group, hence a diminution of the ring-current intensity. Inversely, weak metal–axial ligand π interaction results in longer wavelength for the charge-transfer band and less depopulation of the equatorial

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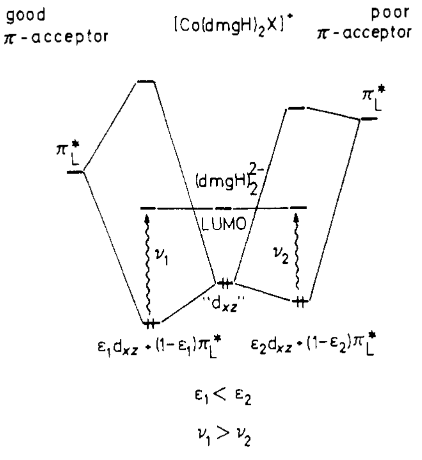

19a 19b

π system and, consequently, larger ring-current effect.

Although ^{13}C NMR data are scarcer due to the low solubility of the studied compounds, some trends similar to those found for ^1H appear. Both types of equatorial carbon atoms are shifted to lower fields than in the free ligand, in agreement with the results of Kohler et al.[28] Also, for the α-carbon atoms of the axial ligand the upfield shifts follow the order 2,6-Me_2pz > 4-NCpy > Me_2pzol, coincident with eq 2. Substituting CN^- for Cl^- produces variations on the signals of both equatorial and axial methylic carbon atoms (for L = 2,6-Me_2pz, compounds **15** and **3**) in the same direction as for the corresponding protons (eq 3) but a change in the chemical shift of C_α opposite to that observed for H_α. This fact is probably not attributable to a failure of the proposed model but due to the fact that C_α lies close to the nodal surface between shielding and deshielding regions, and significative changes in the trans ligand might result in a change of the direction of the effect experienced by those nuclei.

The idea of linking cis and trans influences through conjugation of the π-electron systems of axial and equatorial ligands might be very useful for the understanding of structural and spectral information of a family of related compounds. Thus, the ligand sequences of eq 2 and 3 could be regarded as the order of increasing π-acceptor ability or decreasing π-donor ability of the axial ligands. However, any extrapolation of the relationships presented here must be taken cautiously unless a careful study of other families of coordination compounds with analogous characteristics is undertaken.

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Registry No. **1**, 102920-09-2; **2**, 102920-10-5; **3**, 102920-11-6; **4**, 102920-12-7; **5**, 102920-13-8; **6**, 102920-14-9; **7**, 102920-15-0; **8**, 102920-16-1; **9**, 102920-17-2; **10**, 102920-18-3; **11**, 102920-19-4; **12**, 102920-20-7; **13**, 102920-21-8; **14**, 102940-11-4; **15**, 102920-22-9; **16**, 102920-23-0; $Co(dmgH)_2Cl(H_2O)$, 33896-76-3; $Co(dpgH)_2Cl(H_2O)$, 36795-68-3; $Co(dmgH)_2Br(PPh_3)$, 33988-32-8.

Supplementary Material Available: A table of analytical data for the compounds studied in this paper and listings of isotropic thermal parameters, atomic coordinates of hydrogen atoms, anisotropic thermal parameters, and bond lengths and angles for **1**, **3**, **5**, and **13** (23 pages). Ordering information is given on any current masthead page.

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Stereochemistry and Metal-Centered Rearrangements of Eight-Coordinate Niobium(V) and Tantalum(V) Dithiocarbamates and Monothiocarbamates[1]

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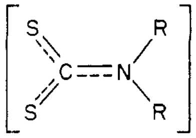
Eight-coordinate niobium(V) and tantalum(V) N,N-disubstituted dithiocarbamato and monothiocarbamato complexes of the type $[Nb(Me_2dtc)_4]Cl$, $[Ta(R^1,R^2dtc)_4][TaCl_6]$ (R^1,R^2 = Me,Me; *i*-Bu,*i*-Bu; Me,*i*-Pr; Me,Ch; Me,Ph), $[Ta(Me,Bzdtc)_4][TaBr_6]$, $[Nb(Me_2mtc)_4][NbCl_6]$, and $[Ta(Me_2mtc)_4][TaCl_6]$ have been prepared by reaction of the metal pentahalides with anhydrous sodium salts of the ligands in dichloromethane. The complexes were characterized by elemental analysis, conductance measurements, and IR and ^1H NMR spectroscopy. Low-temperature ^1H NMR spectra of $[Nb(Me_2dtc)_4]Cl$ and $[Ta(Me_2dtc)_4][TaCl_6]$ are consistent with a dodecahedral *mmmm*-D_{2d} cation, while spectra of the unsymmetrical dithiocarbamato complexes suggest the presence of an equilibrium mixture of *mmmm* stereoisomers that differ in the distribution of methyl groups between the dodecahedral A and B sites. The low-temperature spectra of $[Ta(Me_2mtc)_4][TaCl_6]$ are consistent with the dodecahedral *mmmm*-C_{2v} isomer, in which the four sulfur atoms are clustered in all-cis positions, but the predominant cationic solution species in the case of $[Nb(Me_2mtc)_4][NbCl_6]$ appears to be a *mmmm*-C_s isomer. The kinetics of metal-centered rearrangement have been studied by total line-shape analysis; barriers ΔG^* are 10–12 kcal/mol for the dtc complexes and 14–15 kcal/mol for the mtc complexes. The higher rearrangement barriers for the mtc complexes point to a polytopal rearrangement mechanism.

Introduction

Niobium and tantalum form a variety of complexes with bidentate *N,N*-dialkyldithiocarbamate ligands, R_2dtc^- (**1**; R = Me, Et, CH_2Ph, $^1/_2(CH_2)_4$).[2] Most of these complexes may be assigned to one of the following classes: (i) homoleptic niobium(IV) and tantalum(V) dithiocarbamates of composition $Nb(R_2dtc)_4$ and $Ta(R_2dtc)_5$;[3–6] (ii) pentagonal-bipyramidal oxo, sulfido, and nitrene complexes of the type $MY(R_2dtc)_3$ (M = Nb or Ta; Y = O, S, or NR′, where R′ is alkyl or aryl);[7–13] (iii) pentagonal-



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[1] Presented in part at the Twenty-third International Conference on Coordination Chemistry, Boulder, CO, July 29–Aug 3, 1984; see *Abstracts of Papers*, p 268.

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