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Binuclear Nickel–cobalt Cyano-bridged Complexes Showing Long-range Proton Shielding

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Introduction

Binuclear cyano-bridged complexes have long been known to behave as intermediates in redox reactions, proceeding through internal sphere mechanisms [1–6]. The ability of the bridging cyano group to act as an electron mediator is also evidenced by photochemical [7] as well as Resonance Raman [8] experiments; on the other hand it is a good mediator in the magnetic exchange of binuclear complexes [9–11].

Although the number of bi- and polynuclear cyano-bridged complexes is continuously growing, few cases have been reported in which both linkage isomers $L_mM–CN–M'L_n'$ and $L_mM–NC–M'L_n'$ are isolated and characterized [12]. In this paper we report the synthesis and properties of two such isomers containing the groups Co–CN–Ni and Ni–CN–Co respectively. A remarkable feature of these compounds is the appearance of a long-range magnetic shielding of the methyl protons of the dimethylglyoximato (dmgH) ligand bound to a cobalt atom by the phenyl group of the bis(diphenylphosphino)ethane (dpe) linked to a nickel atom held in the vicinity by a bridging cyano group.

The only previously known examples of cobalt–nickel cyano bridged complexes are |NC(dpe)Co–CN–$NiCl_3$| [13] and $|Ni(CN)_2CoB_2|_n$ [14] (B = aniline). A proposed tetranuclear palladium compound with dpe has also been reported [15].

Experimental

Preparation of Products

|NC(dpe)Ni–CN–Co(dmgH)$_2$Cl| (1)

To a solution of 0.17 g (0.5 mmol) of |Co(dmgH)$_2$(H_2O)Cl| [16] in the minimum amount of acetone, 0.23 g (0.5 mmol) of |Ni(CN)$_2$(dpe)| [17] were added and the mixture stirred at room temperature until a light brown precipitate appeared (approximately 3 hours). The precipitate was filtered, washed with ethanol and ether and air dried (yield 73%). *Anal.* Calcd. for $CoNiC_{36}H_{38}N_6ClO_4P_2$: C, 51.85; H, 4.54; N, 9.61; Cl, 4.14; Co, 6.98; Ni, 7.19. Found: C, 50.45; H, 4.59; N, 10.08; Cl, 4.25; Co, 7.07; Ni, 7.04.

|NC(dmgH)$_2$Co–CN–Ni(dpe)Cl| (2)

A solution of 0.10 g (0.25 mmol) of K|Co(dmgH)$_2$(CN)$_2$|·3.5H_2O [18] and 0.23 g (0.5 mmol) of |$NiCl_2$(dpe)| [17] in the minimum amount of acetone was refluxed for two hours and then cooled to –20 °C. After some minutes a yellow precipitate separated from the solution. The precipitate was filtered, washed with ethanol and ether, and air dried (yield 25%). *Anal.* Calcd. for $CoNiC_{36}H_{38}N_6ClO_4P_2$: C, 51.86; H, 4.54; N, 9.61; Co, 6.98; Ni, 7.19. Found: C, 50.19; H, 4.65; N, 9.56; Co, 6.96; Ni, 7.19.

Spectra

Infrared spectra were obtained from KBr pellets between 4000 and 250 cm^{-1}, with a Beckman IR20A spectrophotometer. The CN stretching region (2300–2000 cm^{-1}) was recorded under moderate resolution conditions and was calibrated against polystyrene film, the estimated accuracy being ± 2 cm^{-1}. Visible and ultraviolet spectra were recorded from freshly prepared solutions in dichloromethane with a Beckman UV-5230 spectrophotometer. ^1H-NMR Fourier spectra were obtained from solutions in deuterochloroform (98% deuterium) using external TMS and $CHCl_3$ signals as standards in a Bruker WP80-SY spectrophotometer.

Analysis

Elemental microanalyses were carried out at the 'Instituto de Química Bioorgánica (CSIC)', Barcelona. Cobalt and nickel were determined by atomic absorption spectroscopy at the 'Servei de Espectroscopia, Universitat de Barcelona'.

Results and Discussion

The new products are slightly soluble in acetone. Conductivity measurements of 10^{-4} *M* solutions show them to be non-electrolytes. Chemical analyses are in good agreement with the proposed formulae and infrared spectra show the presence of both coordinated bis(dimethylglyoximato) and 1,2-bis(diphenylphosphino)ethane ligands, major features including the increased intensity of the band at 1100 cm^{-1}, due to the superposition of the characteristic phosphine band [19, 20] and ν_s(NO) of the cobaloxime, and the bands at 1230 and 1560 cm^{-1} attributed to N=O and C=N stretchings of the coordinated dimethylglyoximato ligand respectively [21–24].

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The appearance of a new C≡N stretching band in the infrared spectra at 2177 and 2180 cm^{-1} for compounds *1* and *2* respectively (Table I), together with a band at nearly the same frequency as in the parent cyano complexes, clearly indicates the existence of both a terminal and a bridging cyano ligand in the compounds, the highest frequency component being attributable to the bridging group [25]. These frequencies are similar to those reported for $Co(dmgH)_2$–CN–$Co(dmgH)_2$ [26] and for Pd(dpe)–CN–Pd(dpe) [15] bridges.

The electronic spectra of the studied compounds (Table II) support the proposed structures. For both compounds the spectra can be interpreted as the superposition of the well assigned spectra of two fragments, $|Co(dmgH)_2XX'|$ [27, 28] and |Ni(dpe)YY'| [17], comprising four types of transitions: (a) Ligand field d–d transitions of the Co(III) ion; (b) ligand field d–d transitions of the Ni(II) ion; (c) $\pi \rightarrow \pi^*$ transitions in the phosphine, and (d) charge transfer transitions in the cobalt–dioxime moiety.

The $^1A_1 \rightarrow {}^1B_2$ ligand field transition of the Ni(II) ion is sensitive to changes in the coordination mode of the cyano group (Table II). The cyano (-CN) ligand is a strong field ligand, and the isocyano (-NC) ligand lies near ammonia in the spectrochemical series [29]. The ligand field effect thus decreases in the order $-CN^- > -NC^- > Cl^-$, and one would expect this transition for compound *1* to be at nearly the same wavelength as in $|Ni(dpe)(CN)_2|$, and at a longer wavelength (though lower than for the dichloro complex) for compound *2*. The $\pi \rightarrow \pi^*$(dpe) bands are well resolved for both complexes as is the charge transfer band of the cobaloxime; the ligand field transition of Co(III) for compound *1* is probably masked by the band of Ni(II).

TABLE I. Cyanide Stretching Frequencies (cm^{-1}) of Bridged Compounds.

Compound	Terminal group	Bridging group	Ref.
$[Ni(dpe)(CN)_2]$	2126	–	this work
$[Co(dmgH)_2(CN)_2]^-$	2140	–	26
$[Co(dmgH)_2CN]_n$	–	2179	26
$[Pd(dpe)CN]_4^{4+}$	–	2185	15
$[NC(dpe)Ni–CN–Co(dmgH)_2Cl]$	2130	2177	this work
$[NC(dmgH)_2Co–CN–Ni(dpe)Cl]$	2134	2180	this work

TABLE III. ^{1}H-NMR Signals (ppm) of the Methyl Groups of Binuclear and Mononuclear Cobaloximes.

Compound	δ	Ref.
$[NC(dpe)Ni–CN–Co(dmgH)_2Cl]$	1.20	this work
$[NC(dmgH)_2Co–CN–Ni(dpe)Cl]$	1.21	this work
$[R(dmgH)_2Co–CN–Co(dmgH)_2R']$	1.99–2.08	30
$Na\{Ag[–CN–Co(dmgH)_2CN]_2\}$	2.22	26
$[Co(dmgH)_2(CN)_2]^-$	2.13	26
$[Co(dmgH)_2(H_2O)X]^a$	2.40–2.43	31
$[Co(dmgH)_2(CN)B]^b$	2.19–2.35	31
$dmgH_2$	1.48	31

^{a}X = Cl^-, Br^-, I^-. ^{b}B = pyridine, 3-Cl–pyridine, piperidine, 4-NH_2–pyridine.

In the proton NMR spectra the broad signal of the aromatic protons of the phosphine at δ = 7.5 ppm is seen, whereas no signal is apparent for the aliphatic protons as is usually found for coordinated dpe. The most interesting features of the spectra are the position of the methyl signal (Table III) of the bis(dimethylglyoximato) group at relatively high fields, and the evolution of the spectra with time (Table IV).

The methylic protons of bis(dimethylglyoximato)-cobalt(III) complexes usually appear at 2.0–2.4 ppm: chemical shift is only slightly sensitive to the nature of the axial ligands bound to cobalt, and to bridge formation by axial cyano groups (Table III). The shift of the methyl signal towards higher fields in the studied complexes is striking at a first glance,

TABLE II. Visible and Ultraviolet Spectra (Wavelengths in nm) and Assignments^a.

Compound	Ni(d → d) $^1A_1 \rightarrow {}^1B_2$	$\pi \rightarrow \pi^\diamond$ (dpe) $A_{1g} \rightarrow B_{2u}$	$\pi \rightarrow \pi^*$ (dpe) $A_{1g} \rightarrow B_{1u}$	Ni (dpe)	Co (d → d) $^1A_{1g} \rightarrow {}^1A_{2g}$	dmgH → Co (CT)
$[Ni(dpe)(CN)_2]$	351(sh)	295(s)	240(s)	320(sh)		
$[Ni(dpe)Cl_2]$	462(w)	280(s)	233(s)	320(sh)		
$[Co(dmgH)_2(CN)_2]^-$					330(w)	240(s)
$[Co(dmgH)_2(NH_3)_2]$					368(w)	247(s)
$[NC(dpe)Ni–CN–Co(dmgH)_2Cl]$	350(w)	295(s)	240(s)	320(w)	[350](w)	240(s)
$[NC(dmgH)_2Co–CN–Ni(dpe)Cl]$	427(w)	271(s)	236(s)	315(sh)	350(w)	242(s)

^{a}Transitions assigned to Ni(II) are labeled according to C_{2v} point group; those assigned to the $Co(dmgH)_2^+$ fragment, according to D_{4h}, and those assigned to dpe, according to the symmetry of the phenyl ring (D_{6h}); s = strong; w = weak; sh = shoulder; CT = charge transfer.

TABLE IV. Time Dependence of the Coordinated dmgH$^-$ Signal of the ^{1}H-NMR Spectra (Chemical Shifts in ppm)[a].

Compound	δ	
	t = 0.5 h	t = 100 h
[NC(dpe)Ni–CN–Co(dmgH)$_2$Cl]	1.20(0.5) 2.18(0.5)	1.21(0.2) 2.13(0.8)
[NC(dmgH)$_2$Co–CN–Ni(dpe)Cl]	1.21(0.8) 2.13(0.2)	1.21(0.2) 2.13(0.8)

[a]The numbers in parentheses are the relative intensities of both signals.

but it can be attributed to the shielding of the methylic protons by the phenyl rings of the phosphine [32]. In Fig. 1 we present a model of the dinuclear complexes calculated with typical bond lengths and angles of cobaloximes [33–38], Ni(dpe)X_2 compounds [39–42] and bridged cyano compounds [43–45], where one can appreciate the proximity of the methyl groups to a phenyl ring. Free rotation about C–CH_3, Co–CN, Ni–CN, or P–C_6H_6 bonds would explain the equivalence of the twelve protons of the cobaloxime moiety at room temperature. The computed position of the nearest proton to the phenyl ring for several geometries of the bridging backbone (from linear to slightly bent) leads to the conclusion that this proton lies in the region of space in which the phenyl ring has a shielding effect and, according to Johnson and Bovely [32], this shielding would produce an upfield shift ranging from 0.8 to 4.0 ppm depending on the extent of the deviation from linearity of the Ni–CN–Co (or Co–CN–Ni) frame.

The methyl signal, on the other hand, loses intensity with time while a new broad signal at 1.50 ppm and another group of signals centered at 2.18 ppm (J = 4.3 Hz) appear (Table IV). The first signal can be attributed to free dimethylglyoxime (δ = 1.48) [31], while the group centered at 2.18 is assigned to the superposition of a singlet of a cobaloxime group far from the phenyl rings [26] and the aliphatic protons' triplet of free dpe (δ = 2.1 ppm; J = 4.1 Hz) [46], indicating bridge cleavage in solution as previously observed for a silver-cobalt cyano bridged complex [26], accompanied by decomposition of the resulting fragments, liberating the uncoordinated ligands. The visible spectra in solution are also substantially altered after several hours but the decomposition products could not be identified.

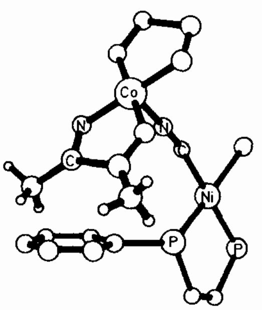

Fig. 1. Molecular model showing the relative position of the methyl and phenyl groups in the binuclear compound *1*. Part of the molecule is omitted for clarity.

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