

Axial Substitution and Bridge Formation by the Cyano Group in Bis(dimethylglyoximato)cobalt(III) Complexes

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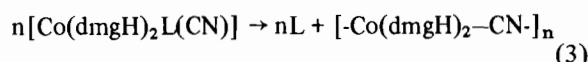
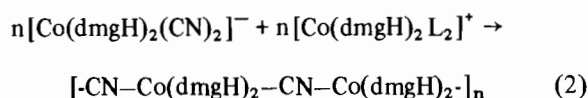
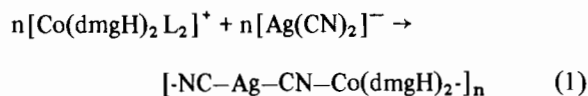
Using the title complexes as building blocks, the formation of polynuclear compounds with cyano bridges of the types Co–CN–Co and Ag–CN–Co was studied. In the first case, a solid polymer was obtained with better conducting properties than the mononuclear compounds, thus confirming the ability of the cyano group to act as a mediator in electron transfer. In the latter case, a variety of compounds was obtained as well as the recently-reported isocyano derivative, due to a rather complex equilibrium existing in aqueous solution.

Introduction

In the synthesis of cyano-bridged dinuclear complexes from a polycyanometallate and a compound of the type $[MLA_5]^{n+}$ or $[MLX(AA)_2]^{n+}$ (where A is a monodentate ligand such as NH_3 , AA is a diamine like ethylenediamine, X is an 'inert' ligand and L is a relatively labile ligand such as H_2O), two major problems usually arise: 1. The *cis-trans* isomerization is an undesired side reaction [1, 2], and 2., The bridge formation is easily produced in the three spatial directions giving place to Prussian blue analogues [3–5].

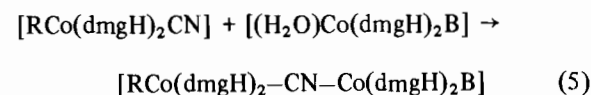
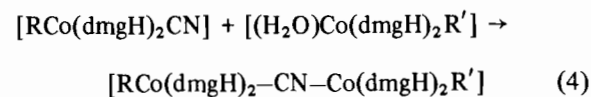
In order to avoid those troubles in the synthesis of linear cyano bridged polynuclear complexes, we have selected the *trans*-bis(dimethylglyoximato)-cobalt(III) derivatives in which the bisdioximato moiety forms a pseudomacrocyclic, planar, almost inert protector group of the equatorial coordination positions of the cobalt atom, leaving the possibility of ligand substitution by the nitrogen end of a cyano complex in the *trans*-axial positions only.

Three types of reactions that could give place to monodimensional polynuclear derivatives have been explored:

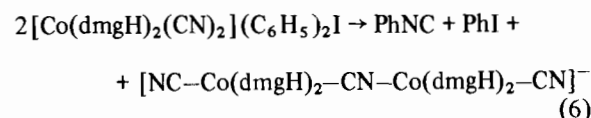


L being a ligand such as H_2O or NH_3 that can be replaced by means of a thermally promoted substitution reaction, as the formation of a cyano bridge is an endothermic process [6–8].

Some similar reactions have been reported for the Vitamin B₁₂ model compounds producing di- or trinuclear complexes [9–12]:



Also a dinuclear compound was obtained by Egen and Krause [13] through an unusual autophenilation reaction:



Experimental

Preparation of Products

The salts of the complex cations $[Co(dmgH)_2L_2]^+$ (L = NH_3 , H_2O) have been obtained by the methods

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described in the literature [14–16], as was the potassium salt of $[\text{Co}(\text{dmgH})_2(\text{CN})_2]^-$ [17]. The double complex salt $[\text{Co}(\text{dmgH})_2(\text{NH}_3)_2][\text{Co}(\text{dmgH})_2(\text{CN})_2]$ has been prepared according to Ablov [18], and the neutral complexes $[\text{Co}(\text{dmgH})_2\text{L}(\text{CN})]$ according to previously described methods [19, 20].

$[\text{Co}(\text{dmgH})_2(\text{H}_2\text{O})_2][\text{Co}(\text{dmgH})_2(\text{CN})_2]$ (I)

1.0 g (2.6 mmol) of $\text{K}[\text{Co}(\text{dmgH})_2(\text{CN})_2] \cdot 6\text{H}_2\text{O}$ were dissolved in water in an ice bath; a solution of 0.9 g (2.5 mmol) of $[\text{Co}(\text{dmgH})_2(\text{H}_2\text{O})_2]\text{Cl}$ in the minimum amount of water was added, and a brown precipitate formed in few seconds. The solution was left in the ice bath with stirring for five minutes and then filtered, washed with ice-cold water and air dried (yield = 90%). *Anal.* Calcd. for $\text{Co}_2\text{C}_{18}\text{H}_{32}\text{N}_{10}\text{O}_{10}$: Co, 17.68; CN^- , 7.80; N(organic), 16.81%. Found: Co, 17.52; CN^- , 7.67; N(organic), 16.72%.

$[\text{Co}(\text{dmgH})_2(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$ (II)

A solution of 1.0 g (5.8 mmol) of $\text{Na}[\text{Ag}(\text{CN})_2]$ in water was mixed with another solution of 2.6 g (5.8 mmol) of $[\text{Co}(\text{dmgH})_2(\text{NH}_3)_2]\text{Cl} \cdot 5\text{H}_2\text{O}$ in 40 ml of water in an ice bath. The mixture was vigorously stirred, until an orange precipitate appeared; the product (yield = 84%) was filtered, washed and air dried. *Anal.* Calcd. for $\text{CoAgC}_{10}\text{H}_{20}\text{N}_8\text{O}_4$: Co, 12.12; CN^- , 10.76; N(organic), 23.61; Ag, 23.60%. Found: Co, 12.10; CN^- , 10.41; N(organic), 23.40; Ag, 23.40%.

$[\text{Ag}(\text{H}_2\text{O})_2][\text{Co}(\text{dmgH})_2(\text{CN})_2]$ (III)

A dispersion of the above product II, 2.0 g in 50 ml of water, was refluxed until completely dissolved. The solution was then concentrated in a rotary evaporator until an orange precipitate formed. The precipitate was filtered and washed with cold ethanol and ether. Yield = 73%. *Anal.* Calcd. for $\text{CoAgC}_{10}\text{H}_{18}\text{N}_6\text{O}_6$: Co, 12.15; CN^- , 10.68; N(organic), 11.50; Ag, 21.49%. Found: Co, 11.52; CN^- , 10.40; N(organic), 11.41; Ag, 21.29%.

$\text{Na}\{\text{Ag}[\text{CN}-\text{Co}(\text{dmgH})_2\text{CN}]_2\}$ (IV)

The double complex salt II was precipitated as stated earlier, and then refluxed until complete re-dissolution of the precipitate. The solution was then concentrated in a water bath at 70 °C until the volume was reduced to one fifth; it was then allowed to cool slowly. After two days, yellow prismatic crystals were formed which were filtered, washed with ethanol and ether, and air dried (yield = 60%). *Anal.* Calcd. for $\text{CoNaAgC}_{20}\text{H}_{28}\text{O}_8\text{N}_{12}$: Co, 14.49; CN^- , 12.79; N(organic), 13.78; Ag, 13.26; Na, 2.83%. Found: Co, 14.78; CN^- , 12.57; N(organic), 13.63; Ag, 12.87; Na, 2.83%.

$[\text{Co}(\text{dmgH})_2\text{CN}]_x$ (V)

To a solution of 0.90 g (2.5 mmol) of $[\text{Co}(\text{dmgH})_2(\text{H}_2\text{O})_2]\text{Cl}$ in 30 ml of water, a solution of 0.12 g (2.45 mmol) of sodium cyanide in 10 ml of water was added. In a few seconds a brown precipitate was produced which was filtered, washed with water, ethanol and ether, and air dried (yield = 70%). *Anal.* Calcd. for $\text{CoC}_9\text{H}_{14}\text{N}_5\text{O}_4$: Co, 18.70; CN^- , 8.25; N(organic), 17.77%. Found: Co, 18.63; CN^- , 8.08; N(organic), 17.71%.

Analytical Determinations

Cobalt was determined titrimetrically with EDTA after digestion of the products with concentrated sulfuric acid for at least three hours. Silver was also determined titrimetrically after digestion of the products. Sodium was determined by the 'Servicio de Espectroscopía de la Universidad de Barcelona' by flame emission in a PYE UNICAM SP 1900 spectrophotometer.

Cyanide was determined by distilling off hydrogen cyanide in 1:3 sulfuric medium over a sodium bicarbonate solution and titrating with silver nitrate. Nitrogen was determined by Kjeldhal's method; as the digestion is carried out in concentrated sulfuric medium, organic nitrogen as well as the amino groups are determined, but the cyano group nitrogen is not included in these analyses.

Spectra

The infrared spectra were recorded in a Beckman IR 20A spectrophotometer in the range 4000–250 cm^{-1} . The spectra in the CN stretching region (2300–1900 cm^{-1}) were obtained under higher resolution conditions, and calibrated against polystyrene film giving an average precision better than 2 cm^{-1} .

Raman spectra were recorded in the 'Laboratoire de Chimie Minérale D, Université des Sciences et Techniques du Languedoc' with a DILOR spectrophotometer equipped with a triple monochromator, using the 5145 Å line of an argon laser (output power = 10 mW) as the exciting source. Spectra of powders in capillary tubes were obtained in all cases in the region 2000–2300 cm^{-1} .

Proton NMR spectra were obtained in a Perkin-Elmer R-12A spectrophotometer using D_2O as solvent (99.8% D) and TMS as external standard.

Other Techniques

Conductivities in solution were measured with a Radiometer COM-3 conductivity bridge, employing 10^{-3} M solutions. Solid state conductivities were measured in the 'Departamento de Física Matemática' of this University with a PAR-TH-136 electrometer on pressed powder disks.

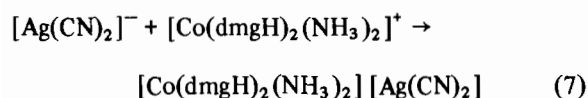
The anionic exchange resins employed were Amberlite IRA-400, and the cationic ones Lewatit S.100/G.1. Thermogravimetric analyses were carried

out in a Perkin Elmer TGS-1 CAHN thermo-balance.

Results and Discussion

Equilibria in Solution

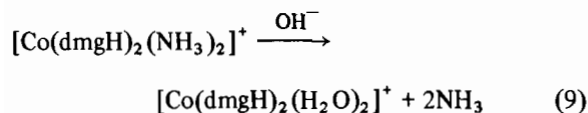
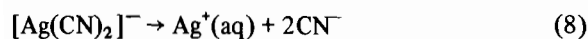
When an aqueous solution of $K[Ag(CN)_2]$ is mixed with another solution of $[Co(dmgH)_2(NH_3)_2]X$, an orange precipitate immediately forms (eqn. 7).



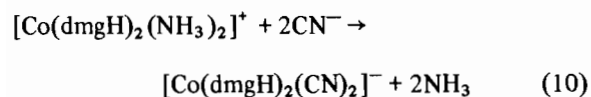
On heating the precipitate is re-dissolved and from the resulting solution the following products can be separately obtained under different conditions (see Preparation of Products): $[Co(dmgH)_2(NC)(H_2O)]$ [23], $Na[NC-Co(dmgH)_2-NC-Ag-CN-Co(dmgH)_2-CN]$, $[Ag(H_2O)_2][Co(dmgH)_2(CN)_2]$ and $[-Co(dmgH)_2-CN]_n$.

These striking results required further experimentation in order to establish the underlying equilibria, which can now be explained through the following reaction steps:

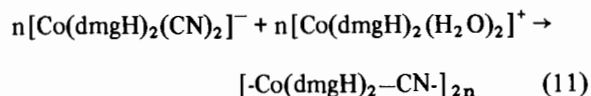
First of all, the dissolution of the sparingly soluble salt precipitated in (7) is promoted by the successive reactions in which both ions are consumed,



The dicyanoargentate ion, although very stable in solution [21], is known to undergo a fast exchange of cyanide ligands in solution [22], the reaction being facilitated by the consumption of cyanide ions in the next steps. The aquation of $[Co(dmgH)_2(NH_3)_2]^+$ at the pH of the reaction mixture (pH = 10) is easily detected by the evolution of ammonia. The evolution of ammonia could also be attributed to the anation reaction (10) which provides the usual synthetic route to the dicyanobis(dimethylglyoximate)cobaltate(III) salts [17].

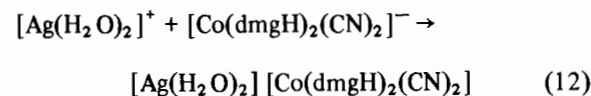


If cyanide and cobalt are present in equimolar amounts, then the brown polymer V is obtained from the solution through the following reaction:

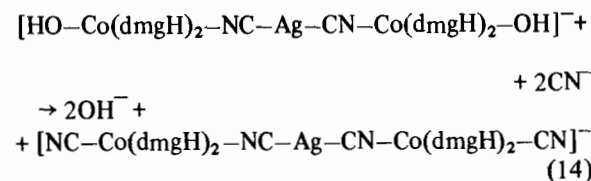
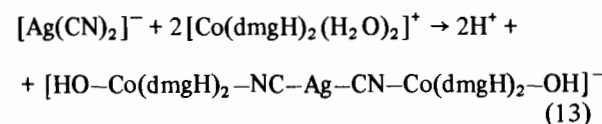


This reaction is indeed produced when both diaquo- and dicyano-cobalt complexes are mixed.

When cyanide and cobalt are present in a 2:1 molar ratio, the product III is obtained by concentration on a rotary evaporator:

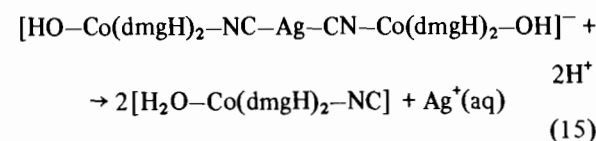


while if the solution is allowed to settle overnight the product IV is separated. The formation of this complex should proceed through an intermediate that could not be isolated in the solid state, but whose existence is probable (see below):

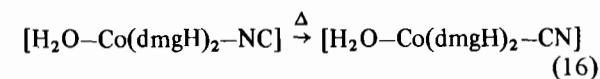


A mixture of dicyanoargentate and diaquobis(dimethylglyoximate)cobalt(III) ions (in 1:2 molar amounts) with an alkaline cyanide, having an overall CN^-/Co molar ratio of 2, yields the product IV, these facts being in agreement with postulated eqns. (13) and (14).

The intermediate proposed in (13) also explains the formation of the isocyano derivative [23] through a reaction involving the cleavage of $Ag-CN$ bonds:



Finally, to complete the picture, the isocyano compound may undergo a thermal isomerization reaction:



The reaction (1), when carried out with the diaquocobaloxime cation, does not permit the isolation of the complex salt, but readily forms a precipitate of the brown polymer V.

Reaction of $[Co(CN)_2(dmgH)_2]^-$ with $[CoL_2(dmgH)_2]^+$, on the other hand, gives place to the

TABLE I. Some Properties of the Reported Complexes. a) Spectra (methyl region) in D₂O (99.8%) solutions. b) Molar conductivities (ohm⁻¹ cm²) of 10⁻³ M solutions.

Compound	ν_{CN} (cm ⁻¹)		¹ H-NMR ^a δ (ppm)	Λ^b
	IR	Raman		
[Co(dmgh) ₂ (H ₂ O)CN]	2186	2185		
[Co(dmgh) ₂ (H ₂ O)NC]	2136	2136		
[Co(dmgh) ₂ (NH ₃)CN]	2150			
[Co(dmgh) ₂ (CN) ₂] ⁻	2140	2150	2.13	195
[Co(dmgh) ₂ CN] _n	2184	2179		
[Ag(H ₂ O) ₂][Co(dmgh) ₂ (CN) ₂]	2140	2150	2.15	216
Na[Ag[-CN-Co(dmgh) ₂ CN] ₂]	2136	2136	2.22	196
		2146		
	2152	2153		
		2173		

insoluble complex salts instead of dinuclear compounds, which show different behaviour upon heating: the diaquo salt gives place (after five minutes of reflux) to the brown polymer V, while the diamine salt after 60 hours produces an oil whose IR spectrum shows an intense band corresponding to terminal CN stretchings (*i.e.*, only partial polymerization is produced). This differential behaviour is consistent with the greater lability of the Co-OH₂ bond relative to the Co-NH₃ one. The polymerization could also be produced on mixing of equimolar amounts of the diaquocomplex and an alkaline cyanide.

Thermogravimetric analyses showed no ligand displacement in the double complex salts, at least until 280 °C. At this temperature a process that overlaps with the decomposition is seen. Thus the solid state polymerizations of the double complex salts could not be studied.

The thermal treatment of the cyano-ligand complexes does not produce bridge formation (eqn. 3), neither in the solid state nor in aqueous suspensions, according to the important *trans*-stabilising effect of the cyano ligand [10, 11].

Characterisation of Compounds

Besides chemical analyses, further chemical and spectral evidence supports the proposed structures for the new complexes.

[Co(dmgh)₂CN]_n

The CN stretching frequency (Table I) appears at higher wavenumbers than for the cyanoamine complex, as expected for bridging cyanides [24]. The long [-Co-CN]_n chain formed must also be responsible for the increase in the solid state elec-

trical conductivity at room temperature on going from K[Co(dmgh)₂(CN)₂] (3.6 × 10⁻¹³ ohm⁻¹ cm⁻¹) to [Co(dmgh)₂CN]_n (9.6 × 10⁻¹⁰ ohm⁻¹ cm⁻¹); a similar result was found by Schneider and Hanack [25] for a linear polymer with pyrazine bridges.

[Ag(H₂O)₂][Co(dmgh)₂(CN)₂]

The recorded spectra (IR, proton NMR) of this compound are fully coincident with those corresponding to the potassium salt of the dicyano ion (Table I). Two sharply defined processes were observed in the thermogravimetric analysis of this compound: the first one at 240 °C with a weight loss of 7.2% (a complete loss of water would represent 7.8%), and the second one at 265 °C with a weight loss of 19.3%; at 310 °C an important process (probably the decomposition of the organic moiety) is finally observed.

Silver salts of the dicyanocobaloximate anion have been reported in the literature [18, 26], although these are clearly different in colour and composition from that reported here.

Na[Ag[-CN-Co(dmgh)₂CN]₂]

This compound contains an anionic complex species, which is retained by an anionic exchange resin and which contains cobalt and silver in a 2:1 molar ratio. Vibrational spectra (Table I) also show evidence for the existence of both terminal and bridging cyano groups. Furthermore, vibrational spectra in the CN stretching region suggest that there is only one kind of bridging cyano groups, as for terminal cyano groups.

From the analysis of the CN stretching bands in both infrared and Raman spectra, two conclusions can be drawn: 1) of the four cyano groups present

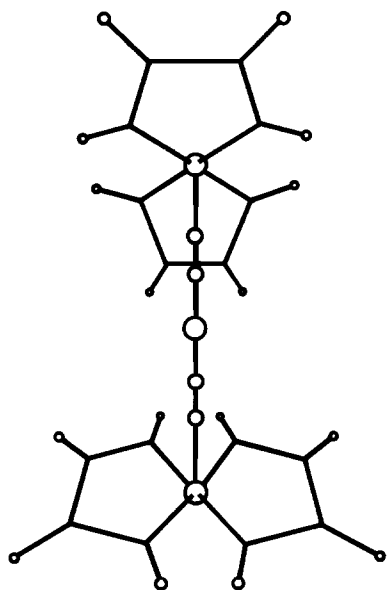


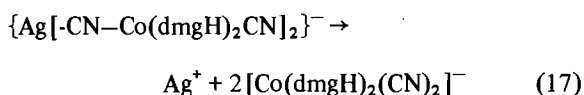
Fig. 1. Proposed structure for $\text{Na}\{\text{Ag}[-\text{CN}-\text{Co}(\text{dmgH})_2\text{CN}]_2\}^-$.

in the complex species per each silver ion, two are terminal and two bridging, and 2) as there are bands appearing in both spectra, the molecule should be non-centrosymmetrical.

In the light of the experimental evidence, a trinuclear structure with both bis(dimethylglyoximate) rings presenting a staggered configuration (point group D_{2d} , see Fig. 1) is tentatively proposed. The proton NMR spectrum of this compound (Table I) shows a single signal in the methyl region, in agreement with the proposed structure although alternative structures could also give place to a single methyl signal.

The crystal structure of this compound could not be determined because it turned opaque during X-ray diffraction data collection. This process is also observed when standing at room temperature for several weeks, but neither a weight loss nor a change in infrared spectrum have been detected.

A decomposition reaction is also evident in solution when studying the evolution of the proton NMR spectrum with time (Table II); the original signal at 2.22 ppm loses intensity while a new signal appears at 2.12 ppm, coincident with the value observed for the dicyanocobaloxime. The decomposition reaction can thus be expressed as

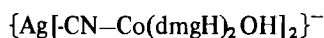


The conductivity measurements in solution (Table II) also support this interpretation.

TABLE II. Behaviour of $\text{Na}\{\text{Ag}[-\text{CN}-\text{Co}(\text{dmgH})_2\text{CN}]_2\}^-$ in Solution. a) Experimental conditions as in Table I. b) Relative intensities in parentheses.

t (h)	δ (CH_3) ^{a,b}	Λ^a
0	2.22	196
2		293
21	2.22(6) 2.12(4)	
400	2.22(5.5) 2.12(4.5)	320

It is obvious that there is no evidence at the present time to elucidate whether the bridging is $\text{Ag}-\text{CN}-\text{Co}$ or $\text{Co}-\text{CN}-\text{Ag}$, although we have formulated it in the first way as the most probable one.



This species could not be isolated, but some evidence has been found of its existence. When potassium dicyanoargentate and diaquocobaloxime nitrate solutions are mixed, the solution becomes acid as could be expected for reaction (13).

The complex species separated by means of an anionic resin in its NO_3^- form is seen to contain silver and cobalt in a 1:2 molar ratio. Titrating the resultant solution (*i.e.*, the cations proceeding from the reaction 13) one mole of protons liberated by each mole of cobalt is found.

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