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Improved Synthesis of Dicyanocobaloximes and the Molecular and Crystal Structure of Potassium Dicyanobis(dimethylglyoximato)cobaltate(III)

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Abstract

An improved method for the preparation of salts of dicyanobis(dioximato)cobaltate(III) ions is presented. It overcomes the usual difficulties associated with the current methods, producing pure products in high yields. The molecular and crystal structure of one of such salts, $K[Co(CN)_2(dmg)_2]\cdot\frac{1}{2}H_2O$, has been determined by X-ray diffraction methods (dmgH = dimethylglyoximato). The compound crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 15.759(3)$, $b = 15.357(3)$ and $c = 13.948(2)$ Å, and $Z = 8$. Each potassium ion is coordinated by the nitrogen end of three cyano ligands, by one oxygen atom from a dioximato group and by three oxygen atoms from hydration water molecules.

Introduction

The anionic complexes *trans*-dicyanobis(dioximato)cobaltate(III) have proven very useful for the synthesis of cyano-bridged polynuclear complexes [1]. The previously existing synthetic route for these compounds [2], however, present several inconveniences: If the synthesis proceeds through method **A**, steps **1**, **2** and **3** (Scheme 1), the yields are usually lower than 30% and the product is often impurified. Step **5**, on the other hand, requires concentration of the resulting solution at low temperatures (lower than 40 °C) and is therefore very slow. In all these processes the infrared spectra of the resulting product indicates the presence of bridging cyano groups as impurities and it has been postulated that the bridge formation is catalyzed by Co(II) [3]. An additional problem is the possible formation of insoluble double complex salts such as $[Co(NH_3)_2(DH)_2][Co(CN)_2(DH)_2]$ [1a], where DH represents a dioximato ligand such as dimethylglyoximato (dmgH) of diphenylglyoximato (dpgH).

We have developed a new, simpler synthetic route which avoids the above problems (method B in Scheme 1), producing pure products with high yields (typically 70%). In this synthetic scheme, the anionic compound can be obtained directly through steps **1** and **2** (method B), or passing through a cyano(ligand)bis(dioximato)cobalt(III) intermediate which can be isolated (steps **3** and **4**). The only potential problem in this procedure is the appearance of cyano-bridged impurities if excess water is added. Through this procedure we have been able to isolate and characterize the potassium salt of the previously unknown diphenylglyoximato complex, and to obtain single crystals of the dimethylglyoximato derivative.

Experimental

Elemental analyses were carried out at the Instituto de Química Bio-Inorgánica (C.S.I.C., Barcelona) with a Carlo Erba 1106 microanalyzer. Infrared and ultraviolet (CH_2Cl_2) spectra were recorded with a Beckman IR-20A and a Beckman UV 5230 spectrophotometer, respectively. ^1H NMR spectra were obtained at 20–25 °C on a Varian XL-200 spectrometer (200 MHz), using D_2O (99.7%) as solvent. Conductivities of 10^{-3} M acetonic solutions of the new compounds were measured with a Radiometer CDM3 conductivity bridge. Weight losses were found by heating the compounds at 120 °C to constant weight.

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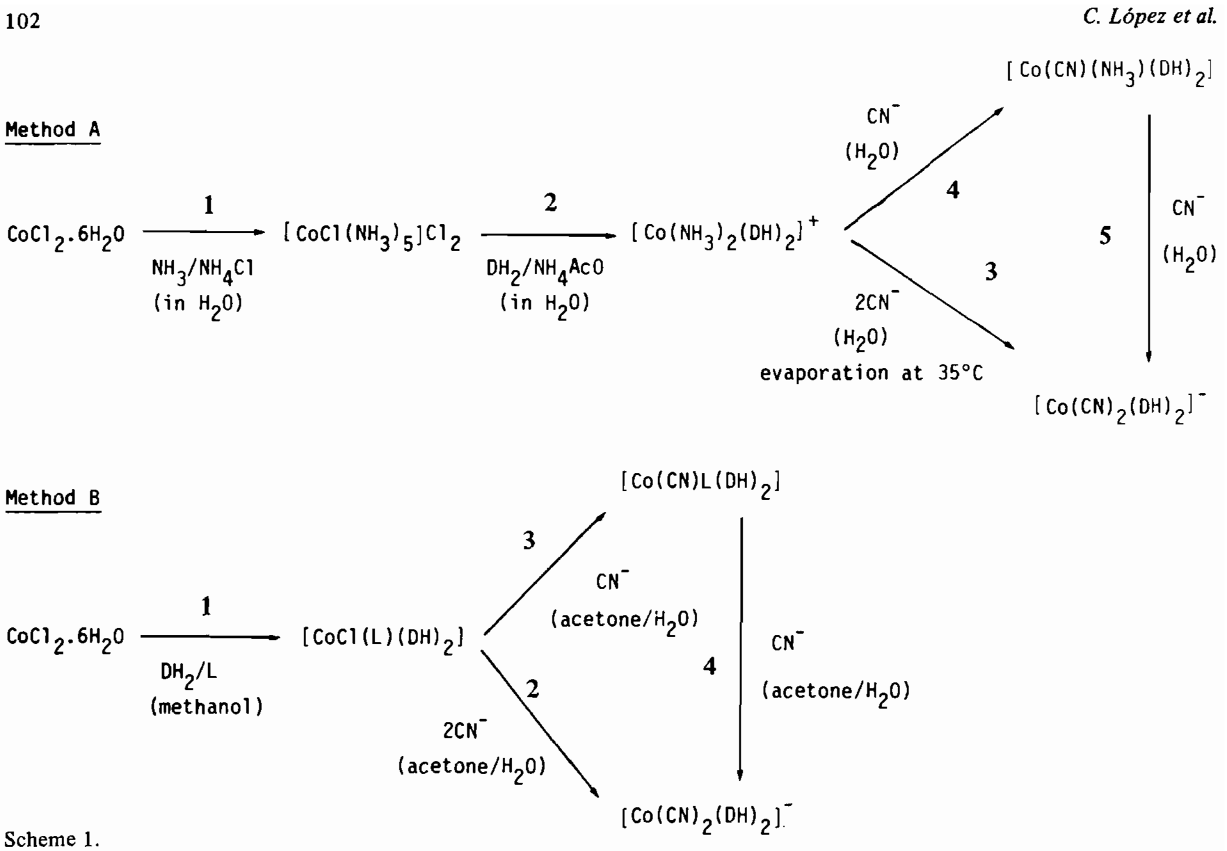

Scheme 1.

Preparation of the Complexes

K[Co(CN)$_2$(dpgH)$_2$]·3H$_2$O (I)

0.2 g (3.0 mmol) of KCN dissolved in water (25 ml) are added to a solution of 1.0 g (1.5 mmol) of [CoCl(dpgH)$_2$(Me$_2$pz)] [4] in acetone (75 ml). The mixture is vigorously stirred at room temperature until a permanent yellow color appears (2 h). Concentration of the solution produces a yellow precipitate which is filtered and washed with acetone (yield 0.68 g, 68%; melting point (m.p.) 243–245 °C, dec.). λ_{max}(CH$_2$Cl$_2$) = 236 nm (log ϵ = 4.60); ν(CN) = 2138 cm^{-1}.

K[Co(CN)$_2$(dmgH)$_2$]·$\frac{1}{2}$H$_2$O (II)

0.7 g (1.6 mmol) of [CoCl(dmgH)$_2$(Me$_2$pz)] [4] are dissolved in acetone (80 ml) and 0.21 g (3.2 mmol) of KCN dissolved in water (10 ml) are added. The mixture is stirred at room temperature until it becomes yellowish (1.5 h). Slow evaporation of the solvent leads to yellow crystals which are removed by filtration and air dried (yield 0.45 g, 73%; m.p. 252–255 °C.) λ_{max} (CH$_2$Cl$_2$) = 238 nm (log ϵ = 4.52); ν(CN) = 2140 cm^{-1}. ^{1}H NMR (D$_2$O): δ = 2.12 ppm (CH$_3$, dmgH).

Crystal Structure Determination and Refinement

A prismatic crystal (0.1 × 0.1 × 0.15 mm) of **II** was selected and mounted on a Philips PW-1000 four-circle diffractometer. The unit cell parameters were determined from 25 reflections ($4° < \theta < 12°$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω-scan technique, scan speed 0.03° s^{-1}, scan width 0.8°. 4102 independent reflections were measured in the range $2° < \theta < 30°$, and 3948 were considered as observed applying the condition $I > 2.5\sigma(I)$. Three intensities were measured every two hours as orientation and intensity control and no significant intensity decay was observed. Lorentz polarization corrections but no absorption corrections were made.

The potassium and cobalt atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from a weighted Fourier synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares methods, using the SHELX76 computer program [5]. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma^2(F_o) + 0.0015|F_o|^2)^{-1}$. Anomalous scattering factors f, f' and f'' were taken from the literature [6]. Methyl hydrogen atoms were computed with an overall isotropic temperature factor and the remaining hydrogen atoms were obtained anisotropically. The final R was 0.056 (R_w = 0.064) for all observed reflections. Final atomic parameters are listed in Table I together with their estimated standard deviations. See also 'Supplementary Material'.

TABLE I. Final Atomic Coordinates ($\times 10^5$ for Co, $\times 10^4$ for all other atoms) of $K[Co(CN)_2(dmgH)_2]\cdot\frac{1}{2}H_2O$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
CoA	87413(5)	1285(6)	23691(6)	CoB	88323(5)	−49619(5)	73288(6)
C1A	8120(5)	601(5)	3423(5)	N1B	9309(5)	−3761(5)	8996(5)
N1A	7737(5)	906(6)	4041(6)	C1B	9157(5)	−4223(4)	8370(5)
C2A	9368(5)	−305(5)	1289(6)	N2B	8327(5)	−6165(6)	5695(5)
N2A	9740(5)	−590(5)	655(5)	C2B	8510(4)	−5705(5)	6291(5)
O3A	9145(5)	−1407(4)	3414(5)	O3B	7177(3)	−4233(4)	7515(4)
N3A	9382(4)	−591(4)	3212(5)	N3B	7682(3)	−4898(4)	7758(4)
C3A	10077(5)	−242(6)	3562(5)	C3B	7450(4)	−5500(5)	8370(5)
C4A	10225(5)	628(6)	3247(5)	O4B	9506(4)	−6473(4)	8216(4)
N4A	9642(4)	906(4)	2653(5)	N4B	8829(4)	−5944(4)	8136(4)
O4A	9676(4)	1693(4)	2268(4)	C4B	8117(5)	−6132(5)	8547(5)
O5A	8337(5)	1665(4)	1309(5)	O5B	10508(3)	−5647(3)	7193(4)
N5A	8102(4)	850(5)	1548(5)	N5B	9978(3)	−5020(4)	6913(4)
C5A	7384(5)	541(6)	1206(6)	C5B	10243(5)	−4406(5)	6338(5)
C6A	7238(5)	−354(7)	1540(6)	O6B	8143(3)	−3492(4)	6365(4)
N6A	7848(4)	−668(5)	2099(5)	N6B	8835(4)	−3981(4)	6495(4)
O6A	7854(4)	−1475(4)	2427(5)	C6B	9537(4)	−3799(4)	6079(5)
C31A	10611(6)	−748(8)	4245(6)	C31B	6584(5)	4478(7)	−1170(6)
C41A	10956(6)	1177(9)	3512(7)	C41B	7990(6)	−6930(6)	9152(6)
C51A	6800(8)	1048(10)	568(7)	C51B	11139(5)	−4321(5)	5984(6)
C61A	6492(6)	−929(9)	1289(8)	C61B	9644(5)	−3053(6)	5416(6)
KA	7650(1)	3039(1)	4085(1)	KB	4809(1)	7009(1)	693(2)
OW1	11572(5)	2833(4)	−2824(5)				
OW2	8237(4)	−2010(4)	291(4)				
OW3	5631(5)	−2807(4)	−1193(5)				

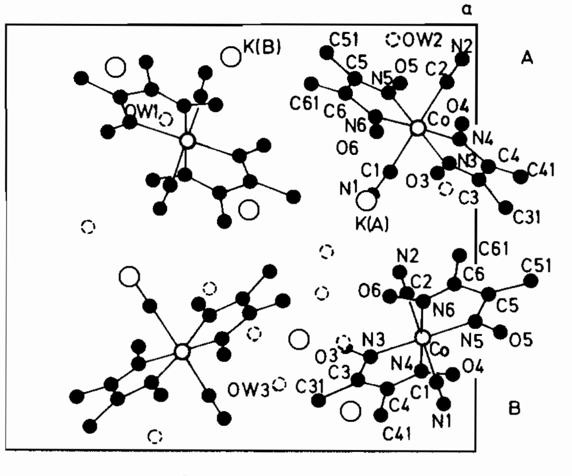

Fig. 1. Projection of the unit cell of $K[Co(CN)_2(dmgH)_2]\cdot\frac{1}{2}H_2O$ (II) along the *b* axis. The large white circles correspond to potassium atoms, and the dashed circles to the oxygen atoms of hydration water molecules.

Crystal Data

$C_6H_{14}N_6O_4CoK\cdot\frac{1}{2}H_2O$ (II), $M = 389.3$, orthorhombic, $a = 15.759(3)$, $b = 15.357(3)$, $c = 13.948(2)$ Å, $V = 3376.4(2)$ Å^3, $P2_12_12_1$, $Z = 8$, $D_x = 1.571$ g cm^{-3}, $F(000) = 1672$. $\lambda(\text{Mo K}_\alpha) = 0.71069$ Å, $\mu(\text{Mo K}_\alpha) = 13.29$ cm^{-1}. Room temperature.

Results and Discussion

The structure of compound **II** (Fig. 1) consists of potassium and *trans*-dicyanobis(dimethylglyoximato)cobaltate(III) ions. Two non-equivalent ions of each sign, labelled A and B, are present in the unit cell. The coordination around the cobalt atoms is approximately octahedral: the four dioximato nitrogens define an equatorial plane, the largest deviation being 0.012(6) Å in the B anion, while the axial cyano groups form an average angle of 90.0(3)° with the equatorial planes. The bond distances and angles within the bis(dimethylglyoximato)cobalt(III) moiety (Table II) are similar to those found for related neutral complexes [7], and the axial Co–C and C≡N bond distances are not significantly different to those in the cyanoaquo complex [8].

The hydrogen bonds between the dioximato groups (Table III, average O- -O distance is 2.481(15) Å) are similar to those previously found [9]. One of the dioximato oxygen atoms (O4A) is also hydrogen-bonded to a hydration water molecule OW3- -O4A^i = 2.788(10) Å), while two are also linked to a potassium ion (O3B to KA, and O5B to KB).

The potassium ions are heptacoordinate (Fig. 2), with bond distances and angles shown in Table III. Each potassium ion is connected to three cyano ligands through their nitrogen atoms, giving place to a chain along the crystallographic *a* axis (Fig. 2).

TABLE II. Selected Bond Distances and Angles in $\mathrm{K[Co(CN)_2(dmgH)_2]\cdot\frac{1}{2}H_2O}$ (II) (e.s.d.s in parentheses)

	Molecule A	Molecule B		Molecule A	Molecule B
Bond distances			Bond angles		
Co–C1	1.909(7)	1.913(7)	C1–Co–C2	177.9(3)	179.8(1)
Co–C2	1.921(8)	1.912(7)	Co–C1–N1	178.0(7)	176.3(7)
Co–N3	1.903(7)	1.912(5)	Co–C2–N2	177.9(7)	177.8(7)
Co–N4	1.896(6)	1.882(6)	N3–Co–C1	90.6(3)	89.2(3)
Co–N5	1.886(7)	1.904(6)	N4–Co–C1	89.1(3)	91.2(3)
Co–N6	1.902(7)	1.899(5)	N5–Co–C1	88.3(3)	90.3(3)
C1–N1	1.152(11)	1.150(10)	N6–Co–C1	91.0(3)	89.7(3)
C2–N2	1.148(10)	1.128(11)	N3–Co–C2	90.6(3)	90.9(3)
C3–N3	1.312(11)	1.310(9)	N4–Co–C2	89.9(3)	88.5(3)
C4–N4	1.308(10)	1.292(9)	N5–Co–C2	90.1(3)	89.6(3)
C5–N5	1.316(10)	1.306(9)	N6–Co–C2	90.1	90.6(3)
C6–N6	1.329(11)	1.280(9)	N4–Co–N3	80.7(3)	81.4(2)
C3–C4	1.426(13)	1.452(10)	N5–Co–N6	82.1(3)	81.2(2)
C5–C6	1.470(14)	1.498(10)	N4–Co–N5	99.1(3)	98.5(2)
N3–O3	1.339(9)	1.338(8)	N3–Co–N6	98.2(3)	98.8(2)
N4–O4	1.324(8)	1.347(8)	C3–N3–O3	122.5(7)	122.5(5)
N5–O5	1.347(10)	1.334(8)	C4–N4–O4	121.7(7)	121.1(6)
N6–O6	1.321(9)	1.336(8)	C5–N5–O5	118.8(7)	120.1(6)
			C6–N6–O6	123.2(7)	121.4(6)
			N3–C3–C4	113.8(7)	112.4(6)
			N4–C4–C3	112.7(7)	113.8(6)
			N5–C5–C6	110.9(7)	110.9(6)
			N6–C6–C5	114.3(7)	113.5(6)

TABLE III. Shortest Non-bonded Distances and Angles for $\mathrm{K[Co(CN)_2(dmgH)_2]\cdot\frac{1}{2}H_2O}$[a]

	Bond distance	KNC or NKN angle		Bond distance	KNC or NKN angle
O3A- - -O6A	2.458(8)		O3B- - -O6B	2.488(8)	
O4A- - -O5A	2.499(8)		O4B- - -O5B	2.478(8)	
OW3- - -O4A^{i}	2.788(8)				
KA- - -N1A^{ii}	3.280(6)	116.2	KB- - -N1B^{vi}	2.836(6)	139.4
KA- - -N2B^{iii}	2.772(6)	166.4	KB- - -N2B^{i}	3.212(6)	91.1
KA- - -N1B^{i}	3.282(6)	92.4	KB- - -N2A^{iv}	2.881(6)	144.2
KA- - -O3B^{i}	2.869(6)		KB- - -O5B^{i}	3.000(6)	
KA- - -OW1^{iv}	2.788(6)		KB- - -OW1^{vii}	3.012(6)	
KA- - -OW2^{v}	2.698(6)		KB- - -OW2^{iv}	2.831(6)	
KA- - -OW3^{v}	2.760(6)		KB- - -OW3^{iii}	2.946(6)	
N1A^{ii}- - -KA- - -N2B^{iii}		116.1	N1B^{vi}- - -KB- - -N2B^{i}		129.6
N1A^{ii}- - -KA- - -N1B^{i}		112.1	N1B^{vi}- - -KB- - -N2A^{iv}		143.8
N2B^{iii}- - -KA- - -N1B^{i}		104.1	N2B^{i}- - -KB- - -N2A^{iv}		74.3

[a] Symmetry code: $i = \frac{3}{2} - x, -y, z - \frac{1}{2}$; $ii = x, y, z$; $iii = x, y + 1, z$; $iv = x - \frac{1}{2}, \frac{1}{2} - y, -z$; $v = \frac{3}{2} - x, -y, \frac{1}{2} + z$; $vi = x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; $vii = \frac{3}{2} - x, 1 - y, \frac{1}{2} + z$.

Each potassium ion is also connected to three oxygen atoms of the hydration water molecules, and to one oxygen atom from a glyoximato group (Table III). The K---N distances are much smaller than the sum of the van der Waals radii [10] (4.35 Å) and the shortest ones (2.77, 2.84 and 2.88 Å) are close to the sum of their ionic (2.84 Å [11]) or covalent (2.72 Å [12]) radii. Also the K- -O distances (2.70–3.01 Å) are smaller than the sum of the corresponding van der Waals radii (4.30 Å [10]) and comparable

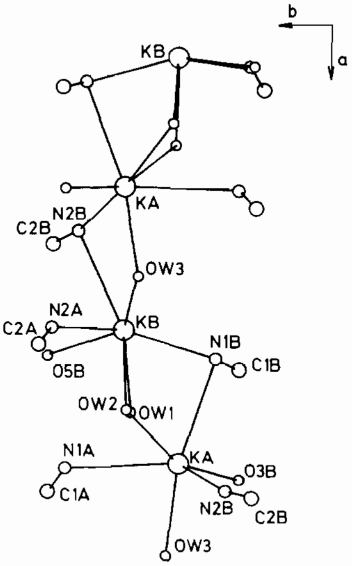

Fig. 2. Shortest non-bonded distances to the potassium ions. Only half unit cell is shown. The upper potassium atoms are related to the lower two by a 2_1 axis. The O3B, as well as the carbon and nitrogen atoms, belong to the dicyanocobaloximate anion (the cobaloxime group is not shown for simplicity), while the OW atoms correspond to hydration water molecules.

to the sum of the ionic (2.73 Å [11]) or covalent (2.69 Å [12]) radii. These non-bonded distances are well within the range observed for simple ionic salts such as KCN or KOH [11], indicating that the interaction between the K^+ ion and the most electronegative atoms in the CN^-, dioximato or H_2O groups is not substantially different to those between the same pair of atoms in the simple ionic salts.

Supplementary Material

Observed and calculated structure factors, anisotropic thermal parameters and hydrogen-atom coordinates are available from the authors on request.

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