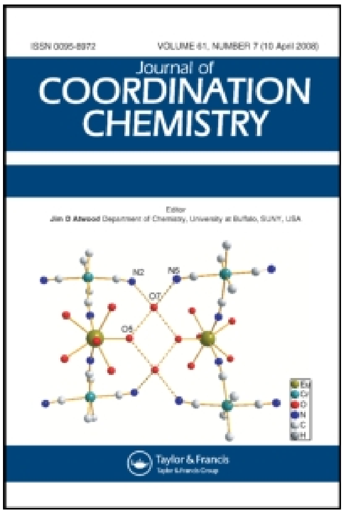

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THE UNEXPECTED SYNTHESES OF $[Co(picam)_3]^3$ SALTS AND THE CRYSTAL STRUCTURE OF $[Co(picam)_3]I_3 \cdot H_2O$ (I)

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THE UNEXPECTED SYNTHESES OF $[Co(picam)_3]^{3+}$ SALTS AND THE CRYSTAL STRUCTURE OF $[Co(picam)_3]I_3{\cdot}H_2O(I)$

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Compounds of composition $[Co(picam)_3]I_3{\cdot}H_2O$(I) and $[Co(picam)_3](ClO_4)_3{\cdot}2H_2O$(II) were unexpectedly obtained while attempting to synthesize [*cis*-$Co(picam)_2(NO_2)_2]^+$ derivatives, using procedures expected to suceed in producing the *cis*-dinitro cation. The structure of the title compound was determined, at which point we realized the nature of the product obtained. (I) crystallizes in the monoclinic system, $P2_1/c$ (No. 14), $Z = 4$, $a = 14.521(7)$, $b = 15.003(4)$, $c = 11.347(4)$ Å, $\beta = 95.01(4)°$, $V = 2462.60$ Å^3 and $d = 2.107$ g–cm^{-3}. F(000) = 1480, R(F) = 0.037 and Rw(F) = 0.044 for 3095 reflections. Data were corrected for absorption obtained from Psi-scans ($\mu = 44.397$ cm^{-1}) and the transmission coefficients ranged from 0.2615 to 0.3878. The cations exist in the lattice as enantiomeric pairs with chiroptical descriptors $\Delta(\delta\delta\lambda)$[fac-$Co(picam)_3]^+$ and $\Lambda(\lambda\lambda\delta)$[fac-$Co(picam)_3]^+$. The analogous perchlorate was obtained also and identified only by its elemental analysis.

Keywords: Cobalt amines; 2-picolyneamine ligands; cobalt iodides; cobalt perchlorates; photochemically induced rearrangements

INTRODUCTION

Note: the ligand picam is the picoline amine ($C_5H_5N\text{-}CH_2\text{-}NH_2$)

Some years ago, Bernal and Cetrullo[1] observed the solution rearrangement of the cation of [*cis*-β-Co(triethylenetetramine)$(NO_2)_2$]I which was found to be catalyzed by I_3^- present in the NaI salt used for its preparation. It was also discov-

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ered that the rearrangement can be induced by long term irradiation of a solution of the pure iodide salt by the laboratory fluorescent lights. For details the reader is referred to the original manuscript. At the time, we dismissed these observations as a curiosity unlikely to reoccur; however, we have recently found that such photo-initiated reactions occur frequently in solutions of related coordination compounds of Co(III) amines in which the counteranion is iodide.

For example, during the past few months we[2] observed that room temperature (*ca.* 22 °C) solutions of $[Co(en)_2oxalato]I$, which are orange, produce golden yellow crystals when allowed to evaporate for many days while exposed to laboratory fluorescent lights. The golden yellow substance was later identified, by its crystal structure as well as by a rational synthesis and elemental analysis, as having composition $[Co(en)_3](Oxalato)\ I{\cdot}1.5H_2O$. Crystals obtained from similar solutions, but kept in total darkness produce the desired $[Co(en)_2oxalato]I$, whose crystal structure was reported by us.[3] Finally, we also observed that solutions of [*cis*-$Co(en)_2(NO_2)I$ produce crystals of $[Co(en)_3]I_3$ under the same conditions of irradiation.[4]

In this paper, we report that we, erroneously, assumed a similar photo-induced reaction occurs during attempts to prepare X-ray quality crystals of [*cis*-$Co(picam)_2(NO_2)_2]I$ from solutions allowed to evaporate under laboratory lights. We now know that the only product obtained from our procedure is, unexpectedly, $[Co(picam)_3]I_3 \cdot H_2O$(I), as shown by its elemental analysis and the structure reported herein. Finally, to demonstrate that the iodide is not responsible for the unexpected product, we carried out the synthesis with $NaClO_4$, instead of NaI, and obtained $[Co(picam)_3](ClO_4)_3 \cdot 2H_2O$(**II**) whose elemental analysis establishes it to be as described. Details are given below.

EXPERIMENTAL

Synthesis and Crystal Growth

(**I**): An aqueous solution of 1 mmol of $[Co(picam)_2Cl_2]Cl$ (0.390g in 30 mL of H_2O) was treated with 2 mmol of $NaNO_2$ (0.140 g), followed by heating on a steam-bath for 30 min, cooling and an excess of NaI added. The large, dark orange crystals which separated were filtered and the filtrate was allowed to stand at room temperature (22 °C) for three days, whereupon crystals suitable for X-ray measurements were obtained. These were collected by filtration, washed with ethanol, ether and air-dried. One of them was selected for the crystallographic study. Several attempts to synthesize the *cis*-dinitro-picam complex failed and, in all cases, the $[Co(picam)_3]^{3+}$ cation was isolated. The reaction was also carried out cold using excess $NaNO_2$, in the presence and absence of light, with the same results as those reported here.

(**II**): synthesis as above, except that instead of NaI, an excess of $NaClO_4$ was added after cooling the solution to room temperature. Yellow needles separated after one day, and were collected, washed with ethanol, ether and air-dried. These crystals were unsuitable for X-ray diffraction studies.

Elemental Analyses

These were carried out by the Analytical Services Laboratory of the University of Kuwait. (**I**): *Anal.* Calcd. for $ICoON_6C_{18}H_{26}$, (%) C = 27.63; H = 3.35; N = 10.74 Found: C = 27.42; H = 3.43; N = 10.85. (**II**): *Anal.* Calcd. for $CoCl_3O_{16}N_6C_{18}H_{28}$ (%), C = 30.12; H = 3.93; N = 11.71. Found: C = 30.43; H = 4.05; N = 11.98.

X-Ray Diffraction

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification of the SDP–Plus software package.[5–6] The crystals were centered with data in the $15° \leq 2\Theta \leq 36°$ range and examination of the cell constants and Niggli matrix (Roof, 1969) and systematic absences clearly showed them to crystallize in a primitive, monoclinic lattice whose systematic absences belong to those of the space group $P2_1/c$ (No. 14). The $F(hkl)_{obs}$ set was corrected for absorption using empirical curves derived from Psi scans of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[7] The structure was solved by direct methods. Refinement, followed by difference maps produced the remaining heavy atoms, including the water of crystallization. The hydrogens of the cation were placed at idealized positions (C-H=N-H=0.95 Å; B=5.00 $Å^2$) and added as a fixed contribution to the calculated structure factors. Details of data collection and processing are listed in Table I. Atomic coordinates are listed in Table II. The asymmetric unit of (**I**) and the packing diagram are shown in Figures 1 and 2. Bond lengths, angles and hydrogen bonded interactions are listed in Table III. All data processing was carried out with the PC version of the NRCVAX programs.[8]

RESULTS AND DISCUSSION

The structure of (**I**) indicated another photochemical rearrangement similar with those previously described.[1–4] The iodide complex was prepared since, depending on the quantum yield, mixtures of the parent dinitro compound and of (**I**) should present in solution, and that the tris-iodide (**I**) being less soluble should

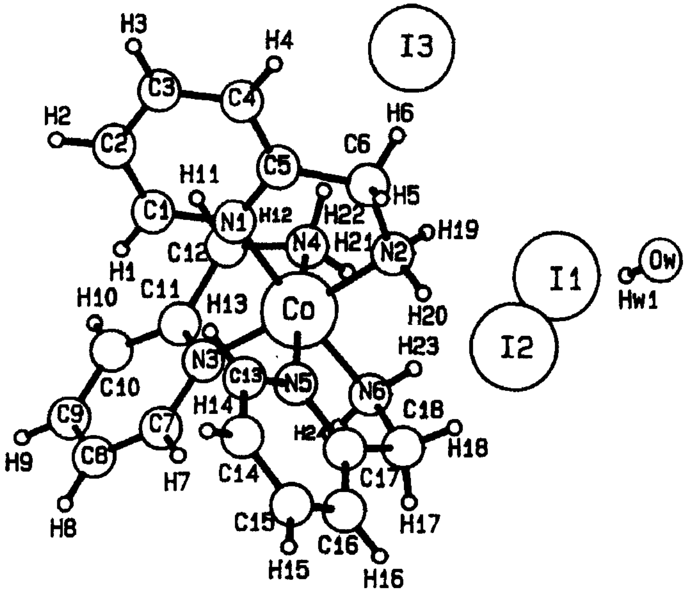

FIGURE 1 The contents of the asymmetric unit in (I). The anions were placed at those positions in which they make the shortest hydrogen-bonded contacts. The water was placed nearest the iodide to which it makes the nearest hydrogen bond.

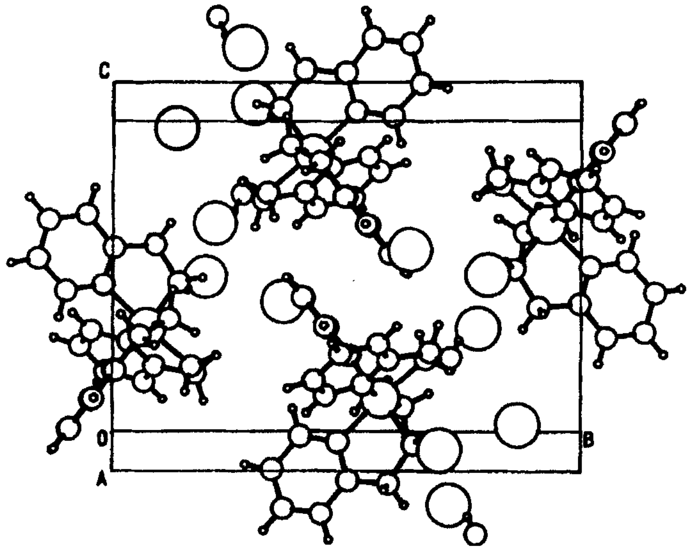

FIGURE 2 The packing of the ions and the waters in the unit cell. This is an a-projection showing the hydrogen-bonding scheme between the ions and the waters of crystallization. Note the inversion center at the center of the cell. Also note that the cations are linked to one another by the agency of the iodides and the water of crystallization with which they make hydrogen bonds.

TABLE I Summary of Data Collection and Processing Parameters for $[Co(picam)_3]I_3{\cdot}H_2(I)$

Space Group	$P2_1/c$ (No. 14)
Cell Constants	a = 14.521(7) Å
	b = 15.003 (4)
	c = 11.347 (4)
	β = 95.01 (4)°
Cell Volume	V = 2462.60 $Å^3$
Molecular Formula	$I_3CoON_6C_{18}H_{26}$
Molecular Weight	782.09 $gm\text{–}mole^{-1}$
Density (calc; z = 4 mol/cell)	2.107 $gm\text{–}cm^{-3}$
Radiation Employed	$MoK_\alpha(\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 44.397\ cm^{-1}$
Relative Transmission Coefficients	0.2615 to 0.3878
Data Collection Range	4° ≤ 2Θ ≤ 50°
Scan Width	ΔΘ = 0.95 + 0.35tanΘ
Total Data Collected	4681
Data Used In Refinement*	3094
F(000)	1480
$R = \sigma\|\|F_O\| - \|F_C\|\|/\sigma\|F_O\|$	0.037
$Rw = [\sigma w(\|F_O\| - \|F_C\|)^2/\sigma\|F_O\|^2]^{1/2}$	0.044
Weights Used	$w = [\sigma(F_O)]^{-2}$

* The difference between this number and the total is due to subtraction of 1587 systematically absent reflections, rebundant data collected to obtain reflections suitable for the absorption correction, were symmetry related, standards or did not meet the criterion that I ≥ 3σ(I).

TABLE II Atomic Parameters x,y,z and Biso* for Compound (I). E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
I1	0.26698(5)	0.13458(4)	0.89952(5)	2.89(3)
I2	–0.03300(5)	0.30098(5)	0.93765(6)	3.86(3)
I3	0.46022(6)	0.28018(5)	1.14685(6)	3.96(3)
Co	0.26373(8)	0.42749(8)	0.82629(10)	1.62(5)
N1	–0.2831(5)	0.4808(5)	1.0498(6)	2.0(3)
N2	0.2113(6)	0.3579(5)	0.9490(7)	2.5(3)
N3	0.3236(5)	0.0026(5)	1.2091(6)	2.2(3)
N4	0.3875(5)	0.3795(5)	0.8640(7)	2.6(3)
N5	0.1397(5)	0.0334(5)	1.2724(7)	2.3(3)
N6	0.2389(5)	0.3315(5)	0.7107(6)	2.0(3)
C1	–0.3245(7)	0.4010(6)	1.0617(9)	2.8(4)
C2	–0.3340(7)	0.3420(7)	0.9676(9)	3.0(4)
C3	0.3026(7)	–0.1355(7)	0.6399(9)	3.1(4)
C4	0.2613(7)	–0.0542(7)	0.6508(8)	3.0(4)
C5	0.2522(7)	0.0033(6)	0.5544(8)	2.5(4)
C6	0.2056(10)	0.4093(8)	1.0577(9)	4.5(6)
C7	0.2807(8)	–0.0469(6)	1.1198(9)	3.1(5)
C8	0.3293(11)	–0.0942(7)	1.0434(10)	4.4(6)
C9	0.5767(12)	0.0914(8)	0.9439(11)	5.1(7)
C10	0.5310(9)	0.0414(8)	0.8562(11)	4.3(5)
C11	0.4146(7)	0.0057(7)	1.2193(9)	2.9(4)
C12	0.4558(7)	0.4425(8)	0.8239(11)	3.9(5)
C13	0.1004(7)	0.5457(7)	0.7981(9)	3.1(4)
C14	–0.0160(8)	0.0695(8)	0.7532(11)	4.0(5)
C15	0.0313(8)	0.0139(9)	0.8343(10)	4.2(5)

TABLE II (*Continued*)

	x	*y*	*z*	*Biso*
C16	−0.0077(7)	−0.0672(7)	0.8587(9)	3.2(4)
C17	0.0932(7)	0.0890(6)	1.1958(8)	2.5(4)
C18	0.1394(7)	0.3224(6)	0.6792(8)	2.7(4)
Ow	−0.1806(7)	0.2220(8)	1.1598(9)	7.1(6)
Hw1	−0.141	0.240	1.113	3.1
H1	0.653	0.385	1.135	3.6
H2	−0.362	0.286	0.977	3.8
H3	−0.309	0.324	0.795	3.9
H4	0.239	−0.037	0.724	3.8
H5	0.142	0.081	0.569	5.4
H6	0.234	0.376	1.122	5.4
H7	0.215	−0.049	1.110	3.9
H8	0.298	−0.129	0.982	5.2
H9	0.542	0.124	0.996	6.1
H10	0.465	0.039	0.847	5.2
H11	0.474	0.483	0.886	4.7
H12	0.508	0.410	0.802	4.7
H13	−0.133	0.415	1.147	3.9
H14	0.011	0.125	0.733	4.9
H15	0.089	0.031	0.872	5.0
H16	−0.024	0.107	1.088	4.0
H17	0.129	0.304	0.599	3.5
H18	0.115	0.279	0.729	3.5
H19	0.249	0.307	0.966	3.3
H20	0.151	0.339	0.921	3.3
H21	0.393	0.324	0.825	3.4
H22	0.398	0.371	0.947	3.4
H23	0.262	0.277	0.744	2.8
H24	0.269	0.345	0.642	2.8

* Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.

TABLE III Bond Distances (Å) and Angles (°) for Compound (I)

A. Bond Distances

Co-N1	1.969(7)	C1-C2	1.385(14)
Co-N2	1.947(7)	C2-C3	1.381(14)
Co-N3	1.957(7)	C3-C4	1.370(15)
Co-N4	1.949(8)	C4-C5	1.389(13)
Co-N5	1.941(8)	C5-C6	1.477(15)
Co-N6	1.960(7)	C7-C8	1.364(15)
N1-C1	1.352(12)	C8-C9	1.359(24)
N1-C5	1.344(11)	C9-C10	1.371(22)
N2-C6	1.462(13)	C10-C11	1.405(15)
N3-C7	1.362(13)	C11-C12	1.499(17)
N3-C11	1.317(13)	C13-C14	1.358(16)
N4-C12	1.471(14)	C14-C15	1.380(19)
N5-C13	1.360(12)	C15-C16	1.379(17)
N5-C17	1.344(12)	C16-C17	1.377(14)
N6-C18	1.465(12)	C17-C18	1.508(13)

TABLE III (*Continued*)

B. Bond Angles

N1-Co-N2	84.5(3)	Co-N6-C18	110.6(5)
N1-Co-N3	93.8(3)	N1-C1-C2	120.2(9)
N1-Co-N4	91.7(3)	C1-C2-C3	120.5(9)
N1-Co-N5	94.8(3)	C2-C3-C4	118.5(9)
N1-Co-N6	175.8(3)	C3-C4-C5	119.7(9)
N2-Co-N3	176.5(3)	N1-C5-C4	121.3(9)
N2-Co-N4	93.2(3)	N1-C5-C6	115.7(8)
N2-Co-N5	88.7(3)	C4-C5-C6	122.9(9)
N2-Co-N6	91.4(3)	N2-C6-C5	112.8(8)
N3-Co-N4	83.8(3)	N3-C7-C8	121.8(11)
N3-Co-N5	94.5(3)	C7-C8-C9	119.1(12)
N3-Co-N6	90.3(3)	C8-C9-C10	120.8(10)
N4-CoN5	173.3(3)	C9-C10-C11	117.1(12)
N4-Co-N6	89.3(3)	N3-C11-C10	122.8(11)
N5-Co-N6	84.3(3)	N3-C11-C12	114.6(8)
Co-N1-C1	125.7(6)	C10-C11-C12	122.5(10)
Co-N1-C5	114.5(6)	N4-C12-C11	110.2(8)
C1-N1-C5	119.8(8)	N5-C13-C14	121.2(10)
Co-N2-C6	112.0(6)	C13-C14-C15	120.3(10)
Co-N3-C7	126.6(7)	C14-C15-C16	118.6(10)
Co-N3-C11	115.0(7)	C15-C16-C17	119.3(10)
C7-N3-C11	118.4(8)	N5-C17-C16	121.7(9)
Co-N4-C12	109.2(6)	N5-C17-C18	115.1(8)
Co-N5-C13	126.3(7)	C16-C17-C18	123.1(9)
Co-N5-C17	114.6(6)	N6-C18-C17	109.1(7)
C13-N5-C17	118.9(8)		

C. Torsion angles

N2	Co	N1	C1	177.5(7)	N2	Co	N1	C5	-1.6(5)
N3	Co	N1	C1	0.6(5)	N3	Co	N1	C5	-178.5(7)
N4	Co	N1	C1	84.4(6)	N4	Co	N1	C5	-94.7(6)
N5	Co	N1	C1	-94.3(6)	N5	Co	N1	C5	86.6(6)
N6	Co	N1	C1	-172.0(7)	N6	Co	N1	C5	8.9(5)
N1	Co	N2	C6	5.3(5)	N3	Co	N2	C6	66.8(6)
N4	Co	N2	C6	96.7(6)	N5	Co	N2	C6	-89.7(6)
N6	Co	N2	C6	-173.9(7)	N1	Co	N3	C7	-99.9(6)
N1	Co	N3	C11	80.7(6)	N2	Co	N3	C7	-161.2(7)
N2	Co	N3	C11	19.4(5)	N4	Co	N3	C7	168.8(7)
N4	Co	N3	C11	-10.6(5)	N5	Co	N3	C7	-4.8(5)
N5	Co	N3	C11	175.9(7)	N6	Co	N3	C7	79.5(6)
N6	Co	N3	C11	-99.8(6)	N1	Co	N4	C12	-71.8(6)
N2	Co	N4	C12	-156.3(7)	N3	Co	N4	C12	21.9(5)
N5	Co	N4	C12	97.2(6)	N6	Co	N4	C12	112.3(7)
N1	Co	N5	C13	14.9(5)	N1	Co	N5	C17	-170.1(7)
N2	Co	N5	C13	99.2(6)	N2	Co	N5	C17	-85.8(6)
N3	Co	N5	C13	-79.4(6)	N3	Co	N5	C17	95.7(6)
N4	Co	N5	C13	-154.0(7)	N4	Co	N5	C17	21.0(5)
N6	Co	N5	C13	-169.3(7)	N6	Co	N5	C17	5.8(4)
N1	Co	N6	C18	59.4(5)	N2	Co	N6	C18	69.9(5)
N3	Co	N6	C18	-113.2(6)	N4	Co	N6	C18	163.0(6)
N5	Co	N6	C18	-18.7(4)	Co	N1	C1	C21	79.9(9)
C5	N1	C1	C2	-1.0(6)	Co	N1	C5	C4	179.6(9)

TABLE III (*Continued*)

C. Torsion angles

Co	N1	C5	C6	–2.5(5)	C1	N1	C5	C4	0.5(6)
C1	N1	C5	C6	178.4(11)	Co	N2	C6	C5	–7.8(4)
Co	N3	C7	C8	179.2(10)	C11	N3	C7	C8	–1.4(7)
Co	N3	C11	C10	–179.1(10)	Co	N3	C11	C12	–3.8(4)
C7	N3	C11	C10	1.5(6)	C7	N3	C11	C12	176.8(12)
Co	N4	C12	C11	–29.0(5)	Co	N5	C13	C14	174.0(10)
C17	N5	C13	C14	–0.9(6)	Co	N5	C17	C16	–174.2(9)
Co	N5	C17	C18	8.6(4)	C13	N5	C17	C16	1.2(6)
C13	N5	C17	C18	–176.0(11)	Co	N6	C18	C17	26.9(4)
N1	C1	C2	C3	1.1(5)	C1	C2	C3	C4	–0.7(6)
C2	C3	C4	C5	0.1(6)	C3	C4	C5	N1	0.0(5)
C3	C4	C5	C6	–177.8(13)	N1	C5	C6	N2	6.8(4)
C4	C5	C6	N2	–175.3(13)	N3	C7	C8	C9	0.5(6)
C7	C8	C9	C10	0.4(7)	C8	C9	C10	C11	–0.4(7)
C9	C10	C11	N3	–0.6(7)	C9	C10	C11	C12	–175.5(14)
N3	C11	C12	N4	21.9(5)	C10	C11	C12	N4	–162.8(13)
N5	C13	C14	C15	–0.8(6)	C13	C14	C15	C16	2.1(6)
C14	C15	C16	C17	–1.8(6)	C15	C16	C17	N5	0.1(6)
C15	C16	C17	C18	177.1(12)	N5	C17	C18	N6	–23.5(5)
C16	C17	C18	N6	159.3(11)					

D. Hydrogen Bonds

Atom 1	Atom 2	Å
I1	H19	2.72
I1	H23	2.77
I1	H24	2.76
I2	Hw1	2.80
I2	H20	2.76
I3	H21	2.80
I3	H22	2.73

crystallize first. That was qualitatively observed with other species,[1,3,4] and quantitatively shown with [Co(en)$_3$](oxalato)I ·1.5H$_2$O.[2]

Duplicate elemental analyses were performed in order to ascertain whether the crystal used in the X-ray study was an aberration, non-representative of the bulk of the other crystals obtained. The results show that, indeed, the bulk of those crystals are compound (**I**) and that our X-ray crystal is a good description of the overall product isolated. Elemental analyses carried out with repeated syntheses are all in agreement that the only species isolated from the above procedure is (**I**). Elemental analyses for (II) also indicate [Co(picam)$_3$](ClO$_4$)$_3$ ·2H$_2$O(**II**) is also the sole product of that reaction. These results were unexpected since we used [*cis*-Co(picam)$_2$Cl$_2$]Cl as our starting material and it should have been converted to the [*cis*-Co(picam)$_2$(NO$_2$)$_2$]Cl by the addition of NaNO$_2$ to the solution of the dichloro cation.

As shown in Figure 1, the cation contains three picam ligands whose pyridine rings occupy *fac* positions around the central Co(III) cation. This arrangement is reasonable since in that configuration all pyridine nitrogens are *trans* to the weaker -NH_2 ligands. In that fashion, the aromatic ring is able to form as strong a pi interaction with the cobalt as possible, while having the terminal -NH_2 non-bonded pair donated to the metal as a sigma bond. Thus, both types of Co-N bond are strengthened; this is illustrated by the fact that all Co-N bonds are of the same length,within *ca.* two standard deviations (*e.g.*, the Co-N(py) bonds are 1.969(7), 1.957(7) and 1.941(8) Å in length, while the Co-N(-NH_2) bonds are 1.947(7), 1.949(8) and 1.960(7) Å. The other parameters within the cation are unremarkable, with the N-Co-N angles deviating somewhat from 90°, as expected.The distances and angles within the amine ligands are well within expected values,given the discrepancy indices recorded in Table I.

The absolute configuration of the cation represented in Figure 1 is $\Lambda(\delta\delta\lambda)$ with torsional angles (Table III) of N1-C5-C6-N2 = 6.8°, of N3-C11-C12-N4 = 21.9° and of N5-C17-C18-N6 = –23.5° and, given the space group, its enantiomorph is also present in the lattice. These torsional angles indicate that the chelate ring is behaving like an ethylenediamine despite the aromatic nature of the pyridine ring and that the four atom fragments listed above are not in the same plane as the plane of the pyridine rings of the picam ligand. However, the one with the 6.8° angle comes closest to being co-planar with its pyridine plane. Further details of the geometry of these fragments are given in Table IIIC.

The iodide anions and the water of crystallization form the usual hydrogen bonds among themselves and with the cations. Some of the shorter hydrogen bonds observed are listed in Table IIID. These shorter contacts document the fact that each of the three iodides form hydrogen bonds with the terminal -NH_2 hydrogens and one of them (I2) also hydrogen bonds to the water of crystallization. There is nothing unusual about the packing contacts observed; the molecule is interesting because of the method by which it was obtained. Together with other recent cases mentioned above this preparation of (I) serves as a warning that crystals of cobalt amine ions bearing ligands such as -NO_2 and oxalate able to transfer electrons to the Co(III), may undergo geometric rearrangements; other complexes may give rise to different chemical species as a result of photo-induced chemical reactions. In the past,we have suggested[1–4] that the transformations observed may be the result of an initial reduction of the robust Co(III) to the labile Co(II), followed by rearrangement of the coordination sphere, resulting in a product which may be kinetic or thermodynamic, depending on the ligands available in solution. Thus far, we have no evidence for a photochemical reaction in this case. However, we find it remarkable that the dichloro compound, $[Co(picam)_2Cl_2]Cl$, which can easily be prepared[9] and is expected to give rise to the dinitro derivative upon reaction with nitrite anions, produced only (**I**) by the procedure given in the Experimental section. However, in the presence of iodide and of perchlorate, we only isolate (**I**), leading to the conclusion that the iodide cannot be responsible for the rearrangement. Unfortunately, we have not obtained usable X-ray quality crystals of $[Co(picam)_2Cl_2]Cl$, of the expected $[Co(picam)_2(NO_2)_2]Cl$ nor of $[Co(picam)_2(NO_2)_2]Br$.

Data on four totally different cobalt amine iodide specimens,[1–4] suggest that several classes of cobalt amine iodide salts are photochemically unstable. Also, depending on solubility and quantum yield (if photochemically unstable) one may obtain crystals of the desired parent compound, its photo-product or both. Our purpose in recording our experiences with photo-induced transformations of compounds of cobalt, in solution, is intended as a warning to the reader who may find it safer to grow crystals of such iodides in the dark, unless interested in exploring the possibility of photo-instability and the products one may derive thereby. Finally, it is conceivable that other products were also formed in our previous studies but, either less efficiently, or because they are more soluble, remained undetected in solution.

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Supplementary Material: Anisotropic thermal parameters (1 page), hydrogen atom coordinates (1 page), torsional angles (1 page) and Structure Factors (17 pages) may be obtained from Ivan Bernal in either printed form or on a PC diskette (send a double sided double density with each request).

References

[1] I. Bernal and J. Cetrullo, *Inorg. Chim Acta.*, **120**, 109 (1986).

[2] I. Bernal, J. Cai and J. Myrczek, *Acta Chimica Hungarica,* **132**, 451 (1995).

[3] I. Bernal, J. Cetrullo, J. Myrczek, J. Massoud and S.S. Massoud, *J. Coord. Chem.*, **30,** 29 (1993).

[4] I. Bernal, J. Myrczek and J. Cai, *Polyhedron*, **12**, 1149 (1993).

[5] TEXRAY-230 is a a modification of the SDP-Plus[6] set of X-ray crystallographic programs distributed by Molecular Structure Corporation, 3200 Research Forest Dr., The Woodlands, TX 77386 for use with their automation of the CAD-4 diffractometer.

[6] SDP-Plus is the Enraf-Nonius Corporation X-ray diffraction data processing programs distributed by B. A. Frenz & Associates, 1140 East Harvey Road, College Station, TX, 77840.

[7] D.T. Cromer and J.T. Waber, "International Tables for X-Ray Crystallography", The Kynoch Press, Birmingham, England (1975); vol. IV, Tables 2.2.8 and 2.3.1, respectively, for the scattering factor curves and the anomalous dispersion values.

[8] The NRCVAX Crystal Structure System, A.C. Larson, F.L. Lee, Y. Le Page, M. Webster, J.P. Charland, & E.J. Gabe, as adapted for PC use by Peter S. White, University of North Carolina, Chapel Hill, N.C., 27599-3290.

[9] S.S. Massoud, unpublished results.