Pergamon

PII: S0277-5387(97)00160-5

Polyhedron Vol. 16, No. 21, pp. 3747–3755, 1997

0277-5387/97 $17.00+0.00

Synthesis and characterization of cobalt(III) azido complexes of some disubstituted pyridine ligands and X-ray crystal structure of *mer*-[Co(3,4-dimethylpyridine)$_3$(N$_3$)$_3$] and *mer*-[Co(3,5-dimethylpyridine)$_3$(N$_3$)$_3$]

Mohamed A. S. Goher,[a]* Najeeb A. Al-Salem[a] and Franz A. Mautner[b]

[a]Department of Chemistry, Faculty of Science, Kuwait University, P.O. Box 5969 Safat, 13060 Kuwait

[b]Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria

(Received 4 February 1997; accepted 14 April 1997)

Abstract—Cobalt(III) azido complexes of some disubstituted pyridine ligands of the type $CoL_3(N_3)_3$ have been prepared and characterized. The complexes gave non-conducting solutions and their solid state and solution electronic spectra are discussed. The IR spectra reveal the asymmetric nature of the azido ligands and the *mer*-formulation was confirmed by the number of Co—N(N$_3$) and Co—N(L) stretching bands observed in the far-IR region. X-ray crystal structure determinations were done for *mer*-[Co(3,4-dimethylpyridine)$_3$(N$_3$)$_3$] (**1**) and *mer*-[Co(3,5-dimethylpyridine)$_3$(N$_3$)$_3$] (**2**). Both compounds contain discrete molecules with approximately octahedral cobalt(III) ion. The Co—N(N$_3$) distances are variable from 1.931(4) to 1.959(4) Å and from 1.944(3) to 1.965(3) Å whereas Co—N(L) bond lengths are from 1.955(3) to 1.994(3) and from 1.973(3) to 1.990(3) Å for **1** and **2**, respectively. The thermal decomposition of complexes (**1**) and (**2**) were investigated drivatographically in nitrogen. Complex (**1**) explodes completely in one step at 175°, whereas complex (**2**) loses one 3,5-DMPy molecule and an azide ion in the first step around 139° and then explodes at 172°. © 1997 Elsevier Science Ltd

Keywords: cobalt(III) complexes; azido complexes; disubstituted pyridines; crystal structures; spectra; thermal decomposition.

The azidopentamminecobalt(III) complex; [Co(NH$_3$)$_5$(N$_3$)](N$_3$)$_2$, was the first azido complex to be structurally characterized in 1964 [1]. Later on many azido–cobalt(III) complexes have been reported in the literature [2–7]. Despite these facts, only a few of them were studied by means of X-ray crystallography.

Recently we started a systematic study of metal azido complexes of disubstituted pyridine derivative ligands and synthesized and structurally characterized those of copper(II) azide with 3,4-dimethylpyridine [8], 3,5-dimethylpyridine [9], 3-ethyl-4-methylpyridine [10], 2,3-dimethylpyridine [11], 2,5-dimethylpyridine [12], 2,6-dimethylpyridine [8] and 2-methyl-5-ethylpyridine [11]. These complexes have different stoichiometries. For example, 3,4-dimethylpyridine forms a 1 : 1 complex; CuL(N$_3$)$_2$, and 3,5-dimethylpyridine gives a complex of the formula CuL$_2$(N$_3$)(NO$_3$), whereas 3-ethyl-5-methylpyridine produces a dimer of the type [CuL$_2$(N$_3$)$_2$]$_2$. Also, 2,3-, and 2,5-dimethylpyridine ligands yield 1 : 1 complexes with copper(II) azide, but 2,6-dimethylpyridine forms a 2 : 3 complex. This later complex of 2,6-dimethylpyridine differs from the monomer 1 : 2 complex of 2,4,6-trimethylpyridine ligand [13], having the same steric hindrance. Thus, it is clear that the stoichiometry of the complexes formed between copper(II) azide and disubstituted pyridine ligands is not only dependent upon the steric hindrance factor but also on the electronic factor as well. As an extension of this work we studied the cobalt(III) azido complexes of such ligands in order to examine the possibility of formation of complexes of stoichiometries different from those of monosubstituted pyridines [7]

---

* Author to whom correspondence should be addressed.

as compared with the copper(II) azide complexes. In the present paper, we describe the results of this study along with the X-ray structures of the 1 : 3 complexes of 3,4-, and 3,5-dimethylpyridines (hereafter abbreviated as DMPy).

EXPERIMENTAL

The organic ligands were purchased from Aldrich and the other chemicals were of analytical grade quality.

Preparation of the complexes

[Co(N_3)$_3$(3,4-*dimethylpyridine*)$_3$] (**1**). This complex was prepared by mixing cobalt(II) nitrate trihydrate (0.95 g, 4 mmol) and 3,4-DMPy (2.14 g, 20 mmol) in acetone (150 cm^3) followed by addition of an aqueous solution of NaN_3 (0.975 g, 15 mmol). To this mixture, an excess of solid $K_2S_2O_8$ was added and the mixture stirred for *ca* 2 h and filtered. The dark green filtrate was allowed to stand in an open beaker at room temperature over several days to produce crystals of good quality of the complex. The yield is about 65% (with respect to Co).

[Co(N_3)$_3$(3,5-*dimethylpyridine*)$_3$] (**2**). Crystals of this complex of a quality suitable for X-ray diffraction measurements were prepared as follows. To a mixture of cobalt(II) nitrate (0.24 g, 1 mmol) and 3,5-DMPy (0.43 g, 4 mmol) in acetone (15 cm^3), was added an aqueous solution (10 cm^3) of NaN_3 (0.26 g, 4 mmol). A saturated aqueous solution of $K_2S_2O_8$ was added and the final mixture stirred for *ca* 2 h and filtered. The filtrate was allowed to stand in a refrigerator over several weeks until complete dryness to deposit dark green crystals. The yield is about 40%.

[Co(N_3)$_3$(3-*ethyl*-4-*methylpyridine*)$_3$] (**3**). This complex was prepared following the procedure given for **2**, except that 3-Et-4-Mepy was used instead of 3,5-DMPy. The yield is about 25%, and the mixture was allowed to stand over two months to deposit the complex.

Trials for preparation of other complexes of different ligands and of different stoichiometries included the change of the cobalt/ligand molar ratios, using of aqueous/DMSO mixture as a medium as well as air oxidation for several days.

Elemental analysis results of the isolated complexes are given in Table 1.

Physical measurements

The IR spectra were measured by a Shimadzu IR-470 and a Bruker IFS-25 model FT-IR spectrophotometer. Solid samples were measured as KBr pellets and liquid ligands as capillary films. Electronic spectra were obtained using Shimadzu UV-3101 PC Scanning spectrophotometer. The ^{13}C NMR spectra were recorded in $(CD_3)_2SO$ using a tube of 10 mm thickness with a Bruker AC 80 MHz spectrophotometer at a probe temperature of 20°C. Chemical shifts are expressed in ppm relative to TMS. The following conditions were used: pulse width 12.0 ms, pulse repetition time 2.818 s. Thermal decomposition was done using DTA 50 Shimadzu Differential Analyzer and TGA-50 Shimadzu Thermogravimetric Analyzer in aluminum pan. The experimental conditions for the DTA runs were as follows: heating rate: 10°C/min, purge gas: dry nitrogen (30.0 ml/min), sample weights: *ca* 6 mg. The instruments were calibrated with standards in the conventional way. The experimental procedures and instruments used for other measurements are as described previously [14].

X-ray crystallography

A modified STOE four circle diffractometer was used for single crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 28 (compound **1**) and 36 (compound **2**) reflections in the 2θ range 10–24°. Data were collected at 295(2) K using graphite crystal-monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å) and the ω-scan technique. The intensities were corrected for Lorentz-polarization effects, intensity decay [Intensity of standard reflec-

Table 1. Analytical data

Complex	Colour	Analysis: (%) found/(calc.) Co	C	H	N
(**1**) Co(3,4-DMPy)$_3$(N_3)$_3$^{a}	Dark green crystals	11.8 (11.6)	50.0 (49.8)	5.5 (5.4)	33.4 (33.2)
(**2**) Co(3,5-DMPy)$_3$(N_3)$_3$	Dark green (black) crystals	11.2 (11.6)	49.7 (49.8)	5.5 (5.4)	33.3 (33.2)
(**3**) Co(3-Et-4-Mepy)$_3$(N_3)$_3$^{b}	Dark green cryst. powder	10.5 (10.7)	52.4 (52.5)	6.2 (6.1)	30.3 (30.6)

[a] 3,X-DMPy = 3,X-dimethylpyridine.

[b] 3-Et-4-Mepy = 3-ethyl-4-methylpyridine.

Table 2. Crystallographic data

Compound	1	2
Molecular formula	$C_{21}H_{27}CoN_{12}$	$C_{21}H_{27}CoN_{12}$
Molecular weight	506.48	506.48
Color	deep green	black
System, Space group	Triclinic, P-1	Monoclinic, $P2_1/n$
a (Å)	9.535(4)	11.292(4)
b (Å)	10.111(5)	19.217(9)
c (Å)	15.126(6)	12.543(5)
α (°)	70.76(4)	90
β (°)	86.54(3)	113.71(3)
γ (°)	63.67(4)	90
V (Å^3)	1227.7(9)	2492(2)
Z	2	4
μ (M6-K$_\alpha$) (mm^{-1})	0.734	0.723
Transmission factors	1.000–0.509	1.000–0.503
D_{calc}/D_{obs} (Mg/m^3)	1.370/1.37(2)	1.350/1.36(2)
Approx. crystal size (mm)	0.50 × 0.35 × 0.20	0.65 × 0.30 × 0.20
2θ range of data collection (°)	2.87–27.50	2.76–27.00
Reflections collected	5799	5848
Independ./refl. R_{int}	5226/0.0350	4951/0.0363
Parameters	317	322
GOF	1.016	1.017
R_1/wR_2	0.0646/0.1471	0.0592/0.1216
Weighting factors: a/b^a	0.858/0.000	0.0609/0.000
Largest peak/hole (eÅ^{-3})	0.569/−0.546	0.319/−0.344

$^a w^{-1} = [\sigma^2(F_o^2)+(aP)^2+bP]$ and $P = [F_o^2+2F_c^2]/3$.

tions dropped continuously during data collection by 14% (compound **1**) and 4% (compound **2**)], and for absorption [15]. Crystallographic data are given in Table 2.

The structures were solved by heavy atom methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to the non-hydrogen atoms in full-matrix least-squares refinements based on F^2. For complex **1**, the occupation factors of 0.720(8) and 0.280(8) of a partially disordered 3,4-dimethylpyridine molecule were also refined by applying one common isotropic displacement factor to disordered carbon atoms C(20) and C(20′). The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The programs DIFABS [15] and SHELXTL/PC [16], were used for computations. Selected bond distances and bond angles are given in Table 3. Positional parameters, anisotropic displacement parameters, hydrogen atom coordinates, a full list of bond lengths and angles and F_o/F_c tables have been deposited as supplementary material.

RESULTS AND DISCUSSION

Despite the many trials for preparation of cobalt(III) azido complexes with 2,3- 2,4-, 2,5-, 2,6-, 3,4-, 3,5-dimethylpyridine and 3-ethyl-4-me-thylpyridine ligands of different stoichiometries, we isolated only complexes of the type $Co(N_3)_3L_3$ of the last three pyridine ligands (Table 1).

In the case of 2,X-dimethylpyridines we could not isolate the solid complexes although dark green coloured solutions were obtained upon addition of $K_2S_2O_8$. The electronic spectra as well as IR spectra (*vide infra*) of these solutions are very similar to those of the isolated solid complexes dissolved in DMF or DMSO, suggesting the formation of the respective complexes in solutions. We tried 2-methylpyridine and 2-chloropyridine ligands and in both cases we could not isolate solid cobalt(III) complexes. Thus the steric hindrance is the main factor which plays the important role in the synthesis of solid cobalt(III) azido complexes of disubstituted pyridine ligands. The isolated complexes, however, are insoluble in water, ethanol, acetone and chloroform, but soluble in DMF and DMSO giving rise to non-conducting solutions in these solvents.

Structure

The structural determinations of Co(3,4-dimethylpyridine)$_3$(N$_3$)$_3$ (**1**) and Co(3,5-dimethylpyridine)$_3$ (N$_3$)$_3$ (**2**) have shown that both complexes have the meridional structure. It can be seen from Figs 1–3 and Table 3 that the coordination around the central cobalt atom in both complexes is approximately

Table 3. Selected bond lengths (Å) and angles (°)

$[Co(3,4\text{-lut})_3(N_3)_3]$ (**1**)			
Co(1)—N(11)	1.931(4)	Co(1)—N(31)	1.949(4)
Co(1)—N(2)	1.955(3)	Co(1)—N(21)	1.959(4)
Co(1)—N(3)	1.994(3)	Co(1)—N(1)	1.995(4)
N(11)—N(12)	1.196(5)	N(12)—N(13)	1.148(5)
N(21)—N(22)	1.187(5)	N(22)—N(23)	1.146(6)
N(31)—N(32)	1.208(6)	N(32)—N(33)	1.149(7)
N(11)—Co(1)—N(31)	94.6(2)	N(11)—Co(1)—N(2)	88.0(2)
N(31)—Co(1)—N(2)	90.5(2)	N(11)—Co(1)—N(21)	90.3(2)
N(31)—Co(1)—N(21)	175.0(2)	N(2)—Co(1)—N(21)	88.6(2)
N(11)—Co(1)—N(3)	176.5(2)	N(31)—Co(1)—N(3)	88.8(2)
N(2)—Co(1)—N(3)	91.2(1)	N(21)—Co(1)—N(3)	86.3(2)
N(11)—Co(1)—N(1)	88.8(2)	N(31)—Co(1)—N(1)	89.6(2)
N(2)—Co(1)—N(1)	176.8(1)	N(21)—Co(1)—N(1)	91.6(2)
N(3)—Co(1)—N(1)	92.0(1)	N(12)—N(11)—Co(1)	123.5(3)
N(13)—N(12)—N(11)	175.4(5)	N(22)—N(21)—Co(1)	120.7(3)
N(23)—N(22)—N(21)	175.7(5)	N(32)—N(31)—Co(1)	121.5(4)
N(33)—N(32)—N(31)	176.2(7)		
$[Co(3,5\text{-lut})_3(N_3)_3]$ (**2**)			
Co(1)—N(21)	1.944(3)	Co(1)—N(31)	1.956(3)
Co(1)—N(11)	1.965(3)	Co(1)—N(1)	1.973(3)
Co(1)—N(3)	1.985(3)	Co(1)—N(2)	1.990(3)
N(11)—N(12)	1.190(4)	N(12)—N(13)	1.155(4)
N(21)—N(22)	1.193(5)	N(22)—N(23)	1.149(6)
N(31)—N(32)	1.192(4)	N(32)—N(33)	1.141(5)
N(21)—Co(1)—N(31)	93.0(2)	N(21)—Co(1)—N(11)	90.9(2)
N(31)—Co(1)—N(11)	176.0(1)	N(21)—Co(1)—N(1)	90.7(1)
N(31)—Co(1)—N(1)	91.9(1)	N(11)—Co(1)—N(1)	89.1(1)
N(21)—Co(1)—N(3)	87.0(1)	N(31)—Co(1)—N(3)	88.2(1)
N(11)—Co(1)—N(3)	91.0(1)	N(1)—Co(1)—N(3)	177.7(1)
N(21)—Co(1)—N(2)	177.8(1)	N(31)—Co(1)—N(2)	88.8(1)
N(11)—Co(1)—N(2)	87.3(1)	N(1)—Co(1)—N(2)	90.5(1)
N(3)—Co(1)—N(2)	91.8(1)	N(12)—N(11)—Co(1)	122.6(3)
N(13)—N(12)—N(11)	175.6(5)	N(22)—N(21)—Co(1)	123.9(3)
N(23)—N(22)—N(21)	176.2(4)	N(32)—N(31)—Co(1)	123.9(3)
N(33)—N(32)—N(31)	175.5(4)		

octahedral. The Co—N(L) bond lengths in compounds (**1**) and (**2**) are consistent with each other. These distances in both complexes, however, are little longer than corresponding values found in the structures of *mer*-$[Co(pyridine)_3(N_3)_3]$ [Co—N(L) from 1.970(1) to 1.986(3) Å] and *mer*-$[Co(4\text{-picoline})_3(N_3)_3]$ (Co—N(L) from 1.961(6) to 1.986(ε) Å] [7] as well as the value of 1.973(1) Å reported for $[Co(DMG)(py)(N_3)]$ (MMG = dimethylglyoximate) [17]. The three azido groups in both complexes are almost linear and asymmetric with δN–N varying from 0.041 to 0.059 Å in **1**, and 0.035 to 0.051 Å in **2** (δN–N is the difference between the N–N distances in an azido group); however in all of them the longer N–N distances is that between the central nitrogen and the nitrogen coordinated to the metal atom. The N–N distances of 1.146(6) to 1.149(7) Å (shorter) and 1.187(5) to 1.208(6) Å in **1**, and 1.141(5) to 1.155(4) Å (shorter) and 1.190(4) to 1.193(5) Å (longer) in **2**, may be compared with the N–N distances reported for the symmetric azide ion with average 1.154(15) Å [18] on one hand, and with typical N–N distances in covalent azides (HN_3 and organic azides) which are 1.248(9) and 1.122(9), respectively [19], on the other hand.

The structures of the title complexes are very similar to that found for *mer*-$[Cr(pyridine)_3(N_3)_3]$ having approximate octahedral geometry around the chromium atom [20]. The Cr—N(L) bond lengths (from 2.013(4) to 2.115(4) Å) as well as the Cr—N(N_3) distances [from 1.999(4) to 2.084(4) Å] in the chromium(III) azido complex are slightly higher whereas the N–N values [from 1.147(7) to 1.155(7) Å (shorter and 1.188(6) to 1.205(7) Å (longer) and the

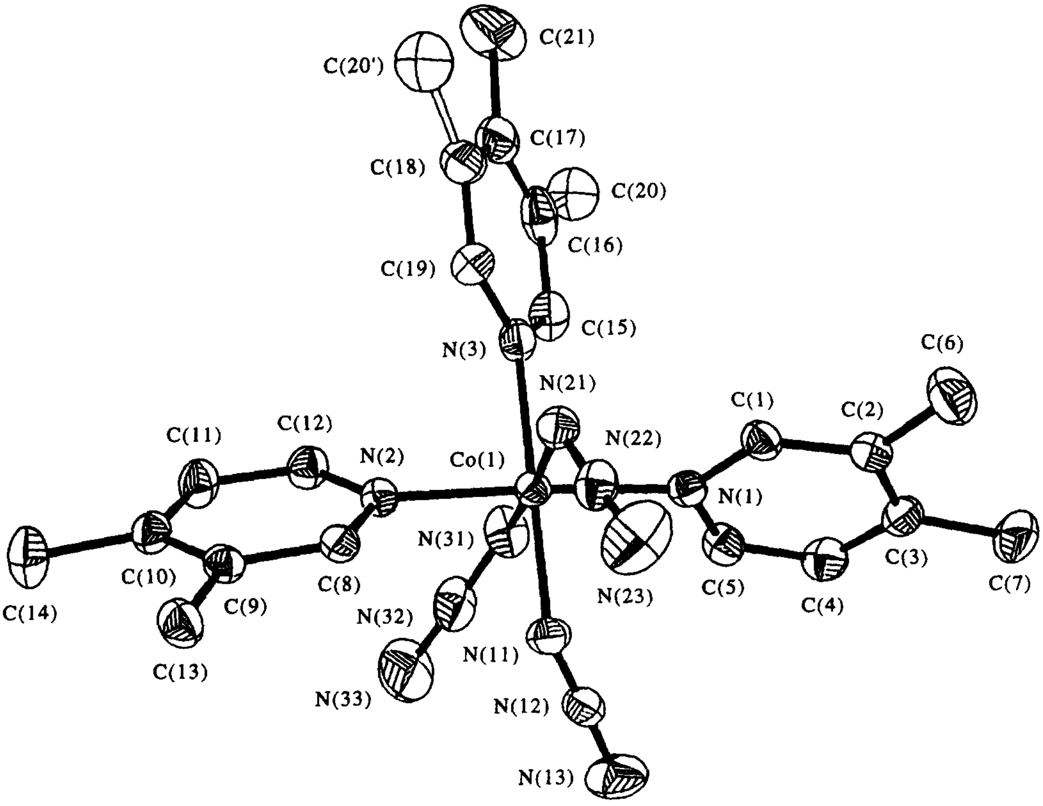

Fig. 1. Molecular geometry and atom labelling scheme of Co(3,4-dimethylpyridine)$_3$(N$_3$)$_3$, (**1**). Open stick bonds indicate disordered methyl groups with partial occupancy. Hydrogen atoms are omitted.

Cr—N—N angles 122.7(3) to 126.8(3)°] are comparable with corresponding values in both of the title complexes. The different N-N distances together with Co—N—N angles which are in general close to 120° have also been found in most of the azido complexes already studied [21–23]. The data given in Table 3 show that an increase in the Co—N distance is accompanied roughly by a decrease in the Co—N—N angle. This observation can be rationalized assuming that a decreasing Co—N interaction makes the azide ligand more similar to the free ion. The repulsion between the electron lone pairs of the bonded azide should increase as the bonding pair becomes less engaged in the bond with the metal atom, therefore increasing the angle between the electron pairs and decreasing the Co—N—N angles. The UV—vis spectra.

The electronic spectra (Table 4 and Fig. 4) of the solid complexes in Nujol mull exhibited three bands in the range 25,900–24,500; 21,100–20,400 and 17,500–114,700 cm^{-1}, which are very close to those found for *mer*-[CoLCl$_3$] and *mer*-[CoL(H$_2$O)$_3$]$^{3+6}$ where L = N-(2-aminoethyl)-1,3-diamino propane or N-(3-aminopropyl)-1,3-diamino propane [24,25]. The first band is due to $^1T_{2g} \rightarrow {}^1A_{1g}$ in a low-spin octahedral cobalt(III) complex which is not affected by lowering of the symmetry. Owing to the high intensity of this band it may be mixed with a charge transfer transition. The lower energy absorption band $^1T_{1g} \rightarrow {}^1A_{1g}$ in an octahedron is expected to split to a very much greater extent in the *mer*- than in the *fac*-isomer [26]. The spectra of [Co(pyridine)$_3$Cl$_3$] and other related CoL$_3$L$'_3$ compounds show two or three components for the $^1T_{1g}$ state (in O$_h$) on the basis of C_{2v} or D_{2h} symmetry [27]. The results given in Table 4 show similar splitting for $^1T_{1g}$ with the band around 20,500 cm^{-1} due to $^1A_2 \rightarrow {}^1A_{1g}$, whereas that around 16,000 cm^{-1} is assigned to $^1E_g \rightarrow {}^1A_{1g}$ [28]. Figure 5 shows the electronic spectrum of a green filtrate obtained from the reaction mixture of cobalt(II) ion, azide ion and 2,5-dimethylpyridine in aqueous/acetone, to which a sufficient amount of solid $K_2S_2O_8$ was added and the final mixture allowed to stand over several days. This spectrum is compared with that of the solid complex [Co(3,4-DMPy)$_3$(N$_3$)$_3$] dissolved in DMF (Fig. 5b). It is clear that the spectra of both solutions are very similar to each other suggesting that a cobalt-(III) azide complex is formed in the case of 2,5-dimethylpyridine ligand. The filtrates obtained from similar reactions of other 2,X-dimethylpyridines gave more or less the same spectrum. Thus these 2,X-dimethylpyridine ligands form similar *mer*- cobalt(III) azide complexes in solutions. The spectra of the solid complexes in DMF solutions exhibit three bands; a higher energy band shifted to 31,300–30,500 cm^{-1}, another band around 17,000 cm^{-1} and a third band

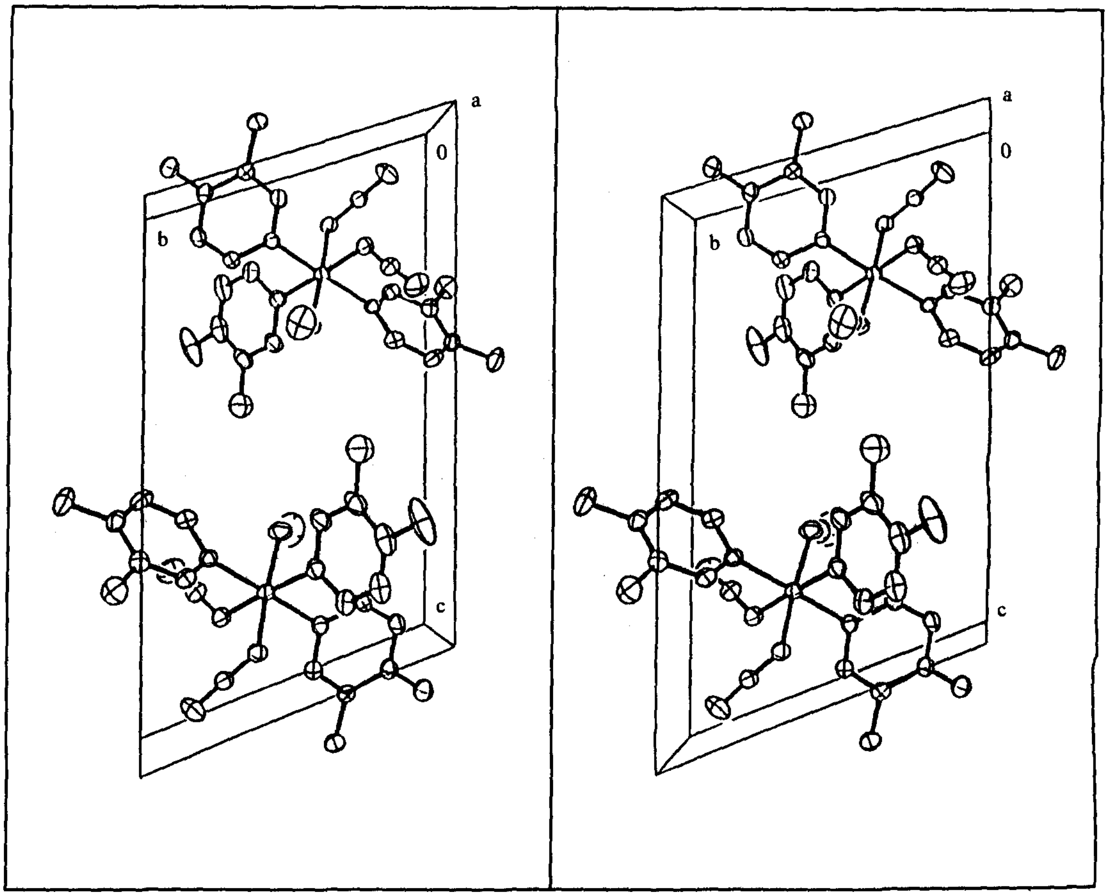

Fig. 2. Stereoview of Co(3,4-dimethylpyridine)$_3$(N$_3$)$_3$, (1), viewed along the *a*-axis of the unit cell. Only one orientation of disordered 3,4-dimethylpyridine molecule is given.

Table 4. Electronic spectral data[a]

Complex	$\lambda_{max}(\xi)$	
	NM[b]	DMF
1	25,900 vbr[c,d] 20,400 sh[e] 16,650 br	30,950(4500) 17,500(227) 15,500(238) 14,700 sh
2	25,700 vbr 20,800 sh 16,530 br	31,300(3480) 17,300(173) 15,740(217) 14,530(217)
3	24,500 vbr 21,050 sh 16,000 br	31,150(3600) 17,100(195) 15,500(220) 14,350 sh

[a] In cm^{-1}.
[b] Nujol mull.
[c] v = very
[d] br = broad
[e] sh = shoulder.

which is shifted to lower energies when compared with the solid state spectra. The latter band appears as a plateau or as a splitted band (Table 4) in the three complexes. Similar observations have been reported for *mer*-[CoL$_3$(N$_3$)$_3$] complexes where L = pyridine or monosubstituted pyridine ligand [7].

IR spectra

The IR spectra (Table 5) of the complexes exhibit very strong absorption bands just above 2000 cm^{-1}, and medium to strong bands in the region 1350–1280 cm^{-1}, associated with the ν_{as}(N$_3$) and ν_s(N$_3$) modes, respectively. The region for ν_{as} mode is very narrow and at lower frequencies (2020–1995 cm^{-1}) than corresponding region (2100–2000 cm^{-1}) reported for *mer*-[CoL$_3$(N$_3$)$_3$] complexes of monosubstituted pyridines [7]. That the δN–N values for *mer*-[CoL$_3$(N$_3$)$_3$] complexes with L = pyridine and 4-picoline are little higher than δN–N values found in the present complexes may explain the difference in their absorption regions. However, according to the ν_{as}(N$_3$) *vs* δN–N relationship [29], the δN–N values in the title com-

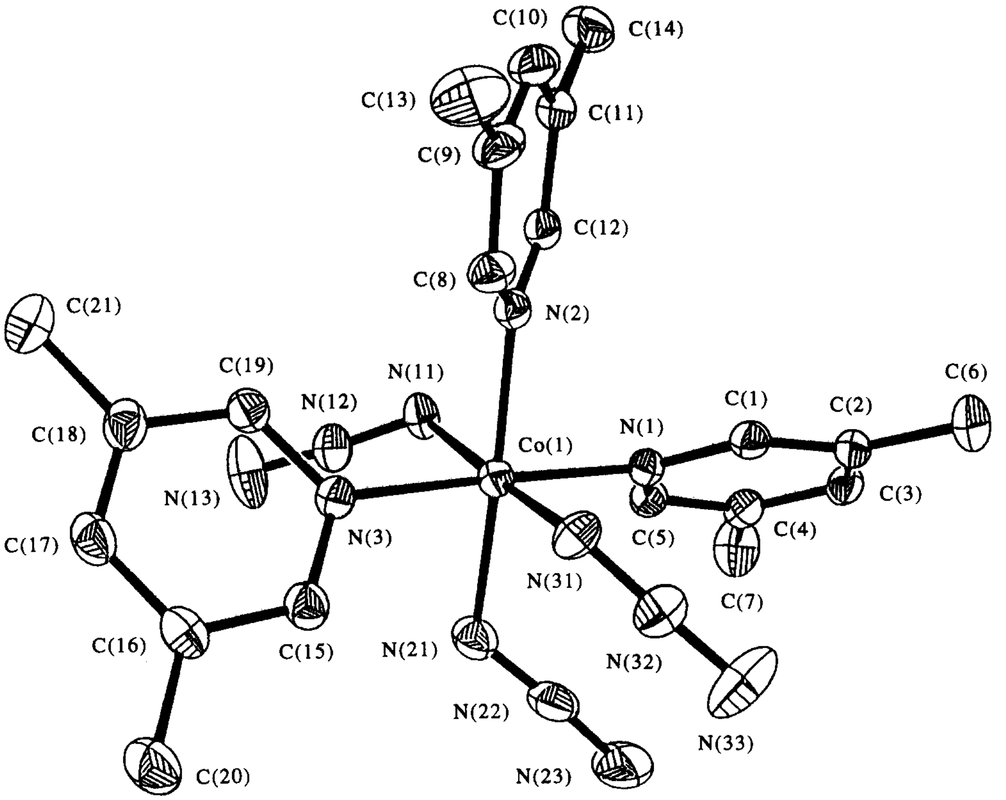

Fig. 3. Molecular geometry and atom labelling a scheme of Co(3,5-dimethylpyridine)$_3$(N$_3$)$_3$, (2). Hydrogen atoms are omitted.

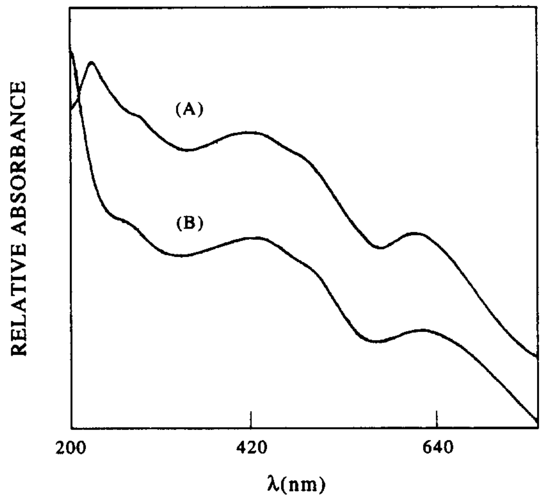

Fig. 4. Electronic spectra of solid complexes: (A) Co(3,5-dimethylpyridine)$_3$(N$_3$)$_3$; (B) Co(3-ethyl-4-methylpyridine)$_3$(N$_3$)$_3$.

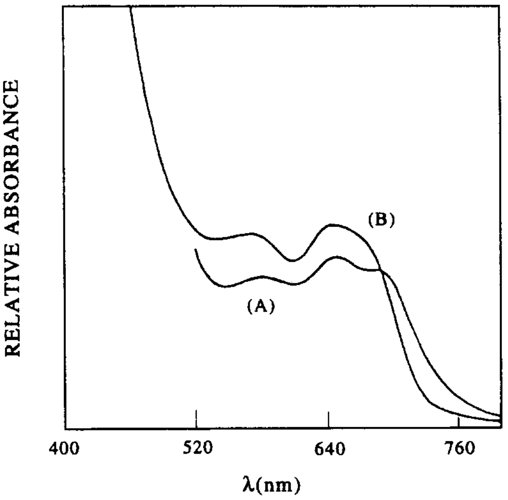

Fig. 5. Electronic spectra of: (A) Filtrate of a reaction mixture containing 2,5-dimethylpyridine; (B) Co(3,4-dimethylpyridine)$_3$(N$_3$)$_3$ dissolved in DMF.

plexes suggest that at least two bands around 2040, 2060 cm^{-1} and 2035, 2050 cm^{-1} should appear in the spectra of complexes (**1**) and (**2**), respectively. It appears, therefore, that the other ligand influence the positions of the ν_{as}(N$_3$) mode irrespective of the δN–N values. For the series of *mer*-cobalt(III) azide complexes of pyridine, 4-picoline, 3,5-DMPy and 3,4-DMPy the ν_{as} bands appear at 2040; 2040–2000; 2020–2000 and 2010–1995 cm^{-1}, respectively. IR spectra of the filtrates of 2,X-dimethylpyridine mixtures exhibit very strong absorption bands in the vicinity of 2040–2000 cm^{-1}, very similar to those of the solid complexes. This give another evidence that these 2-X-disubstituted pyridines form cobalt(III) azide com-

Table 5. Azide and cobalt-ligand vibration frequencies in the complexes

Frequency (cm^{-1}) 1	2	3	Assignments
2010 vs	2020 vs	2005 vs	$\nu_{as}(N_3)$
2000 vs(sh)	2000 vs	1995 vs(sh)	
1347 m	1342 m	1350 wm	$\nu_s(N_3)$
1282 ms	1285 s	1280 ms	
613 w	610 w	618 w	$\delta(N_3)$
595 wm	590 wm	590 wm	
430 m	425 m	435 m	νCo—N_3
392 s	397 m	405 ms	
345 ms	340 ms	350 ms	
280 m	277 m	285 m	μCo—N(L)
260 ms	252 ms	260 ms	
235 s	230 s	240 s	

w = weak, m = medium, s = strong, v = very, sh = shoulder.

plexes that can be formulated as *mer*-[CoL$_3$(N$_3$)$_3$] in their solutions. The asymmetric nature of azido ligands in the solid complexes was evidenced from the appearance of the $\nu_s(N_3)$ mode which is IR-inactive for symmetrical azides. In the region 500–200 cm^{-1}, three bands assigned as νCo—N$_3$ vibrations and other three bands below 280 cm^{-1} due to νCo—N(L) vibrations have been observed in the spectra of all complexes, similar to those reported for other *mer*-[CoL$_3$(N$_3$)$_3$] complexes [7]. This result supports the meridional formulation of the title complexes.

^{13}C *NMR spectra*

In order to gain more information on the geometry of the synthesized complexes, particularly complex **3**, and since the solubility of them all permits, the ^{13}C NMR chemical shifts were obtained in (CD$_3$)$_2$SO. The ^{13}C NMR spectrum of complex **1**, consists of signals at 151.6; 150.76; 149.09; 132.94 and 124.96 ppm, attributed to pyridine carbons 2, 6, 4, 3 and 5, respectively. The first two can be interchanged. The signals at 17.59 and 15.69 ppm are attributed to methyl carbons at C(4) and C(3), respectively. For [Co(3,5-DMPy)$_3$(N$_3$)$_3$] complex **2**, the NMR spectrum consists of signals at 147.43 [pyridine C(2) and C(6)], 137.15 [pyridine C(4)], 130.58 [pyridine C(3) and C(5)] and 14.84 ppm due to methyl carbons. These signals in fact appear as multiplets indicating that the three pyridine rings are not magnetically equivalent as a result of their meridional arrangements in the complex molecules. For facial arrangement, the signals are expected to appear as singlets. The same trend is observed for complex **3**. Its ^{13}C NMR spectrum consists of multiplet signals at 156.89 [pyridine C(2)], 155.84 [pyridine C(5)], 154.33 [pyridine C(4)], 144.05 [pyridine C(3)], 131.27 [pyridine C(5)], 28.25 (—CH$_2$—), 22.96 [methyl carbon at C(4)], and 18.46 ppm (methyl carbon at —CH$_2$—CH$_3$). The ^{13}C NMR spectra, therefore confirm the meridional arrangement in the three isolated cobalt(III) complexes and supports the results obtained from their electronic spectra and other tools.

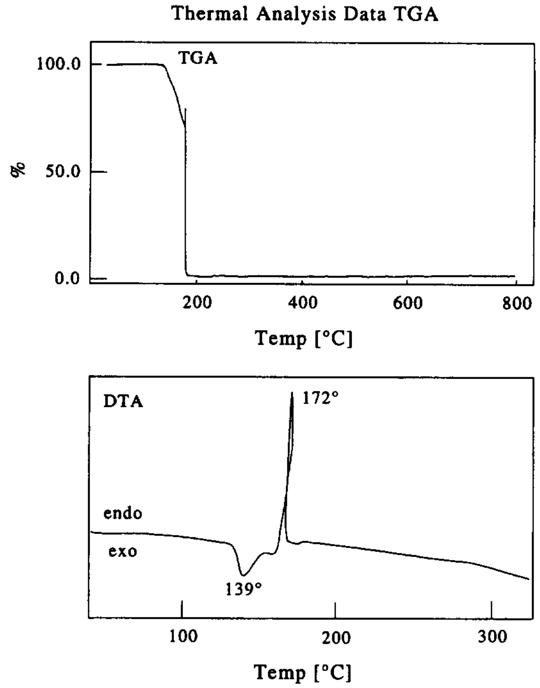

Fig. 6. Thermal decomposition of [Co(3,5-dimethylpyridine)$_3$(N$_3$)$_3$], (**2**).

Thermal decomposition

The thermal decomposition of complexes (**1**) and (**2**) have been investigated in nitrogen atmosphere and the TGA and DTA curves for **2** are reproduced in Fig. 6. The first step of the thermal decomposition of complex (**2**) consists of a loss of one 3,5-DMPy molecule and an azide ion (loss of weight (%): experimental 30.52 and theoretical 29.47) in the range 140–178°C. The reduced [Co(3,5-DMPy)$_2$(N$_3$)$_2$] residue explodes completely around 178°C. The DTA curve shows the first step as an endotherm with T_{max} = 139°C and $\Delta H = -27.02$ kJ/mol, followed by an exotherm (Fig. 6) with T_{max} = 172°C. ΔH for this exothermic process is 35.01 kJ/mol. The thermal decomposition of complex (**1**) does not contain the thermal reduction of cobalt(III) as in case of complex (**2**), but it consists of only one process; the explosion of the complex with a 100% loss of weight. The DTA curve of this complex is a simple one and shows only an exotherm at T_{max} = 175°C with ΔH = 76.78 kJ/mol.

Acknowledgements—Financial support by the Kuwait University Research Administration Project (No. SC 077) and the Department of Chemistry General Facility Projects

(Analab) are gratefully acknowledged. The authors thank Prof. Kratky for the use of the STOE diffractometer.

REFERENCES

1. Palenik, G. H., *Acta Cryst.*, 1964, **17,** 360.
2. Staples, P. J. and Tobe, M. I., *J. Chem. Soc.*, 1960, 4812.
3. Buckingham, D. A., Olsen, I. I. and Sargeson, A. M., *Inorg. Chem.*, 1967, **6,** 1807; Massoud, S. S., *Polyhedron*, 1994, **13,** 1467.
4. Pearson, R. G., Henry, P. M. and Basolo, F., *J. Am. Chem. Soc.*, 1957, **79,** 5378; Tobe, M. L. and House, D. A., *J. Chem. Soc., Dalton Trans.*, 1989, 853.
5. Linhard, M. and Flygare, H., *Z. Anorg. Allg. Chem.*, 1950, **262,** 328.
6. Linhard, M., Weigel, M. and Flygare, H. Z., *Z. Anorg. Allg. Chem.*, 1951, **263,** 233; Massoud, S. S., *Polyhedron*, 1994, **13,** 3127, and refs therein.
7. Goher, M. A. S., Wang, R.-J. and Mak, T. C. W., *Polyhedron*, 1992, **11,** 829.
8. Mautner, F. A. and Goher, M. A. S., *Polyhedron*, 1994, **13,** 2141.
9. Mautner, F. A. and Goher, M. A. S., *Struct. Chem.*, 1994, **5,** 171.
10. Mautner, F. A. and Goher, M. A. S., *Polyhedron*, 1996, **15,** 1139.
11. Goher, M. A. S., Al-Salem, N. A. and Mautner, F. A., *Polyhedron*, 1996, **15,** 4513.
12. Goher, M. A. S., Mautner, F. A. and Al-Salem, N. A., *Polyhedron*, 1997, **16,** 2339.
13. Goher, M. A. S. and Mautner, F. A., *Polyhedron*, 1996, **15,** 5.
14. Goher, M. A. S., Wang, R.-J. and Mak, T. C. W., *J. Coord. Chem.*, 1996, **38,** 151.
15. Walker, N. and Stuart, D., *Acta Cryst.*, 1983, **A39,** 158.
16. SHELXTL/PC V 5.03, Siemens Analytical Automation Inc., Madison, WI (1995).
17. Elliot, H., Hathaway, B. J. and Slade, R. C., *Inorg. Chem.*, 1966, **5,** 669.
18. Agrell, I., *Acta Chem. Scand.*, 1970, **24,** 1247.
19. Yoffe, A. D., Development in Inorganic Chemistry (Ed. G. B. B. Colburn) Vol. I, p. 72. Elsevier, New York (1996).
20. Goher, M. A. S., Abu-Youssef, M. A. M. and Mautner, F. A., *Z. Naturforsch.*, 1992, **74b,** 139.
21. Cruickshank, D. W. J., Phillippini, G. and Mills, O., *J. Chem. Soc., Chem. Commun.*, 1972, 101.
22. Padmanabhan, V. M., Balasubramanian, R. and Muralidharan, K., *Acta Cryst., Section B*, 1986, **24,** 1638.
23. Castellano, E. E., Piro, O. E., Punte, G., Amalvy, J. L., Varetti, E. L. and Auonino, P. J., *Acta Cryst., Section B*, 1982, **38,** 2239.
24. Gainsford, A. R. and House, D. A., *J. Inorg. Nucl. Chem.*, 1970, **26,** 3977.
25. Couldwell, M. A. and House, D. A., *J. Inorg. Nucl. Chem.*, 1971, **33,** 2583.
26. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, p. 308, Elsevier, New York (1968).
27. Laier, T., Schaffer, C. E. and Springborg, J., *Acta Chem. Scand.*, 1980, **34A,** 343.
28. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, 2nd edn. p. 477, Elsevier, New York (1984).
29. Agrell, I., *Acta Chem. Scand.*, 1971, **25,** 2965.