Inorganica Chimica Acta, 142 (1988) 43–50

Studies on The Metal–Amide Bond. XX*. A Structural Comparison of an Unusual Dimeric Cobalt(III) Complex, *fac*-[$Co_2(bpen)_3$]·$12H_2O$, with the Free Ligand *N,N'*-Bis(2'-pyridinecarboxamide)-1,2-ethane, bpenH_2

FREDERICK S. STEPHENS** and ROBERT S. VAGG

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2109, Australia

(Received April 10, 1987)

Abstract

The crystal and molecular structures of the ligand bpenH_2 (*N,N'*-bis(2'-pyridinecarboxamide)-1,2-ethane) and its deprotonated dimeric cobalt(III) complex *fac*-[$Co_2(bpen)_3$]·$12H_2O$ have been determined by single-crystal X-ray diffraction methods. Crystal data: (a) bpenH_2, $C_{14}H_{14}N_4O_2$, orthorhombic, space group *Pccn*, $a = 9.638(1)$, $b = 15.288(1)$, $c = 8.684(1)$ Å, $Z = 4$; (b) $Co_2(bpen)_3$·$12H_2O$, $C_{42}H_{60}N_{12}O_{18}Co_2$, triclinic, space group $P\bar{1}$, $a = 11.128(3)$, $b = 14.316(5)$, $c = 16.466(4)$ Å, $\alpha = 92.02(2)°$, $\beta = 95.21(2)°$, $\gamma = 99.30(2)°$, $Z = 2$.

The structures were refined to R 0.034 and 0.053 for 1064 and 7748 independent reflexions, respectively. The bpenH_2 molecule has a space group imposed centre of symmetry, with the amide group adopting a *trans* configuration in the closely planar picolinamide moiety. The cobalt complex is dimeric in which three bpen ligands, acting each as a bis(N_2-bidentate), bridge the two metal atoms. Each cobalt atom is octahedral with Co–N_{py} 1.944(3) and Co–N_{am} 1.933(3) Å. The Co··Co separation is 5.493(1) Å. The symmetry of the dimeric molecule is D_3 which is consistent with that indicated from solution NMR studies.

Introduction

The ambivalent coordinating ability of the carboxy-amide group has been well demonstrated by the large number of transition metal complexes that have been reported for the picolinamide-based ligand *N,N'*-bis(2'-pyridinecarboxamide)-1,2-ethane (bpenH_2) and its substitutional derivatives [1]†. Depending on the synthetic conditions employed these ligands commonly act as N_4-tetradentates, necessitating amide-group deprotonation, or as bridging NO bis-bidentates if in the non-deprotonated form [2, 3]. Monomeric deprotonated complexes form readily with bivalent nickel, copper and palladium [1], but the only isolated Co(II) complex to demonstrate this behaviour is that of the relatively inflexible ligand bpbH_2 [4], based on 1,2-diaminobenzene.

During an attempt to prepare the deprotonated cobalt(II) complex of bpenH_2, red diamagnetic crystals formed in the reaction solution after it had been left standing for several days. Thermogravimetric studies were consistent with the formulation $Co_2(bpen)_3$·$12H_2O$ and the proton NMR spectrum of this complex suggested that in solution it possesses high symmetry. We report here the crystal structure of this complex together with that of the free ligand for comparative purposes.

Experimental

Crystals of the free ligand, bpenH_2, were obtained by recrystallization from aqueous ethanol. The cobalt complex was obtained as diamagnetic red crystals from the aqueous reaction solution, containing cobalt(II) acetate and the bpenH_2 ligand, in the mole ratio (1:1), after standing for several weeks. The thermogravimetric analysis of these crystals, summarized in Table I and carried out on a Stanton-Redcroft Model TG-750 Thermobalance in conjunction with a direct read-out recorder, is in accord with the formula $Co_2(bpen)_3$·$12H_2O$. The ^1H NMR spectrum for the complex in DMSO, recorded on a Varian XL-200 spectrometer, is shown in Fig. 1.

Structure Analysis

Crystal data, data collection and refinement details are summarized in Table II. For bpenH_2 with $Z = 4$ the molecule is required to possess $C_i(1)$ or $C_2(2)$ symmetry. Its structure was solved

---

*For Part XIX, see ref. 1.

**Author to whom correspondence should be addressed.

†See also other papers in this series.

0020-1693/88/$3.50

TABLE I. Thermogravimetric Analysis Results

Temperature range (°C)	Product lost	Weight Loss (%)		Metal (%)	
		Calc.	Found[a]	Calc.	Found[b]
40–135	$12H_2O$	19.0	19.1		
310–485	3bpen	70.7	70.3		
	Total loss	89.7	89.4	10.3	10.6

[a]Final weight loss corrected for uptake of oxygen. [b]Assuming Co_3O_4 to be the remaining solid.

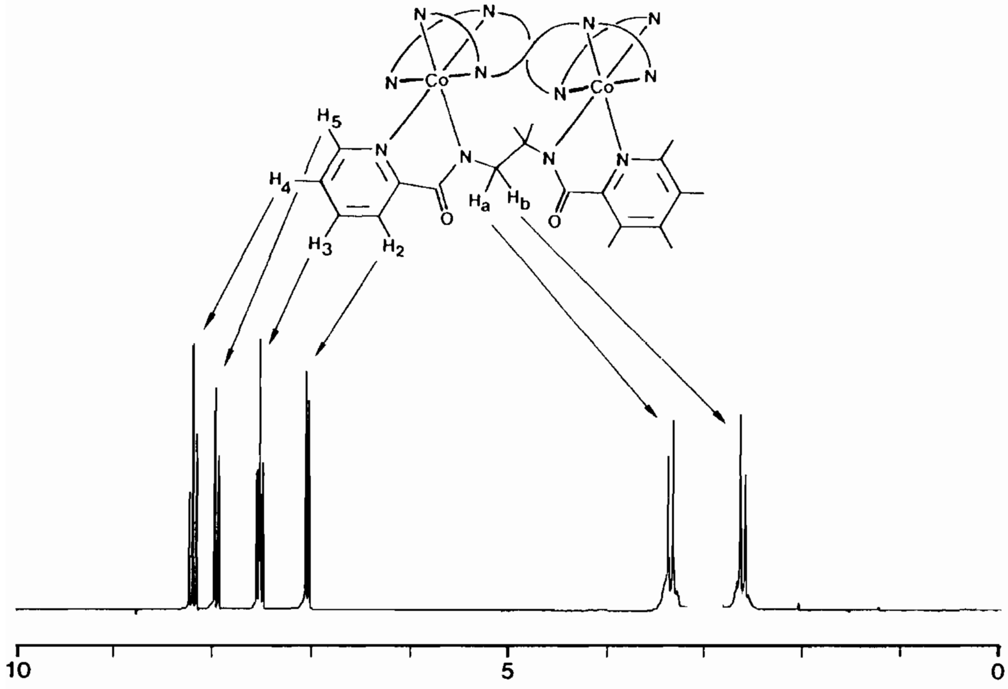


Fig. 1. ^1H NMR spectrum of $[Co_2(bpen)_3]$ in DMSO. The H_2O signal has been removed for clarity.

TABLE II. Summary of Crystal Data, Data Collection and Structure Refinement

Compound	$bpenH_2$	$Co_2(bpen)_3 \cdot 12H_2O$
Colour	colourless	red
Crystal habit	plates lying on (010) with pinacoids {100} and {001}	multifaced, major pinacoids {010}, {011}, $\{01\bar{1}\}$ *ca.* 0.27 × 0.44 × 0.40 mm
Crystal data		
Formula	$C_{14}H_{14}N_4O_2$	$C_{42}H_{60}N_{12}O_{18}Co_2$
M_r	270.3	1138.9
Crystal system	orthorhombic	triclinic
Space group	*Pccn* (No. 56)	$P\bar{1}$ (No. 2)
a (Å)	9.638(1)	11.128(3)
b (Å)	15.288(1)	14.316(5)
c (Å)	8.684(1)	16.466(4)
α (°)		92.02(2)
β (°)		95.21(2)

(continued)

TABLE II. *(continued)*

γ (°)		99.30(2)
U (Å^3)	1279.5	2574.5
D_m (by flotation)		1.46
Z	4	2
D_c (g cm^{-3})	1.403	1.469
μ (cm^{-1})	7.6 (Cu Kα)	7.5 (Mo Kα)
F(000)	568	1188
Intensity Data		
Instrument	Siemens AED	Nicolet XRD P3 [6]
	4-circle diffractometers	
Radiation	Cu Kα	Mo Kα
Temperature	R.T.[a]	R.T.[a]
$2\theta_{max}$ (°)	46.5	55.0
Absorption corr.	no	yes [6]
Total no. reflexions	1219	11871
No. $I > 3\sigma(I)$	1064	7748
Refinement		
Computer	UNIVAC 1106	FACOM 340S
Programs	written by F.S.S.	
Scattering factors	neutral atom [7]	
Least-squares		
matrices	full	4 block
anisotropic	all non-hydrogen atoms	
H atoms	refined isotropically	included, except waters; not refined
weighting scheme	counting statistics	$w = (5.0 + 0.1\|F_o\| + 0.004\|F_o\|^2)^{-1}$
R	0.034	0.053
R' (= $\{\Sigma w\Delta^2/\Sigma w\|F_o\|^2\}^{1/2}$)	0.052	0.074
Final Δ map (ρe Å^{-3})	<|0.15|	<|0.6|

[a] Room temperature

TABLE III. Final Atomic Coordinates (fractional: $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms) for bpenH$_2$

	x	y	z
N(11)	1191(1)	1039(1)	4623(1)
C(11)	−155(1)	1117(1)	4272(1)
C(12)	−1079(1)	1613(1)	5121(2)
C(13)	−588(2)	2060(1)	6398(2)
C(14)	788(2)	1980(1)	6782(2)
C(15)	1632(1)	1463(1)	5873(2)
C(01)	−671(1)	640(1)	2865(1)
O(1)	−1887(1)	712(1)	2457(1)
N(1)	273(1)	163(1)	2115(1)
C(1)	−76(2)	−279(1)	699(1)
H(12)	−208(2)	166(1)	481(2)
H(13)	−125(2)	242(1)	703(2)
H(14)	121(2)	228(1)	766(2)
H(15)	258(2)	141(1)	614(1)
H(N1)	112(2)	12(1)	253(1)
H(1a)	55(2)	−80(1)	57(2)
H(1b)	−106(2)	−50(1)	76(2)

[a] e.s.d.s in parentheses.

using MULTAN80 [5] which showed the molecular symmetry to be $C_1(\bar{1})$. The structure of the cobalt complex was solved by the heavy-atom method. Difference maps, used to locate the lattice water molecules, revealed that some disorder with them was present. Only nine of the twelve molecules could be considered to have full occupancy. Partial occupancy was assigned to seven other peaks on the basis of their approximate peak heights. Final atomic coordinates for all atoms of bpenH$_2$ and for the non-hydrogen atoms of Co$_2$(bpen)$_3$·12H$_2$O are given in Tables III and IV respectively.

Discussion

Tables V and VI give the bond lengths and angles for the ligand and the coordination molecule, respectively. Figure 2 shows perspective drawings [8] of the two structures together with atom labelling. Table VII lists for both structures close intermolecular contacts and proposed hydrogen bonding in the lattices.

TABLE IV. Final Atomic Coordinates (fractional $\times 10^4$) for Non-hydrogen Atoms of $Co_2(bpen)_3 \cdot 12H_2O$[a]

	x	*y*	*z*
(a) The $Co_2(bpen)_3$ molecule			
Co(1)	2976.3(4)	2307.2(4)	907.5(3)
Co(2)	2294.2(4)	2352.0(4)	4245.5(3)
N(a11)	1623(3)	2649(3)	202(2)
N(a1)	2800(3)	3430(2)	1535(2)
N(a2)	3633(3)	3462(2)	3692(2)
N(a21)	4502(3)	2699(3)	4957(2)
C(a11)	1208(4)	3396(3)	493(2)
C(a12)	188(4)	3703(4)	128(3)
C(a13)	−408(5)	3218(4)	−580(3)
C(a14)	33(5)	2456(4)	−881(3)
C(a15)	1044(4)	2182(3)	−483(3)
C(a01)	1937(4)	3883(3)	1237(2)
O(a1)	1697(3)	4656(2)	1504(2)
C(a1)	3617(4)	3915(3)	2226(2)
C(a2)	3014(3)	3925(3)	3041(2)
O(a2)	5251(3)	4685(2)	3798(2)
C(a02)	4698(4)	3933(3)	4019(2)
C(a21)	5232(4)	3460(3)	4724(2)
C(a22)	6377(4)	3775(4)	5114(3)
C(a23)	6782(4)	3285(4)	5760(3)
C(a24)	6035(5)	2519(4)	6004(3)
C(a25)	4893(4)	2238(4)	5592(3)
N(b11)	4261(3)	3067(3)	372(2)
N(b1)	4355(3)	2022(2)	1607(2)
N(b2)	3840(3)	1495(2)	3672(2)
N(b21)	2424(3)	1228(3)	4825(2)
C(b11)	5389(4)	3073(3)	745(3)
C(b12)	6426(4)	3576(4)	468(3)
C(b13)	6285(5)	4085(4)	−227(3)
C(b14)	5128(5)	4074(4)	−614(3)
C(b15)	4128(4)	3557(3)	−295(3)
C(b01)	5442(4)	2450(3)	1441(2)
O(b1)	6454(3)	2338(3)	1797(2)
C(b1)	4356(4)	1318(3)	2223(2)
C(b2)	4764(3)	1731(3)	3102(2)
O(b2)	4062(4)	−58(3)	3576(3)
C(b02)	3635(4)	619(3)	3871(3)
C(b21)	2782(4)	447(3)	4525(3)
C(b22)	2410(5)	−421(4)	4800(3)
C(b23)	1642(6)	−504(4)	5426(4)
C(b24)	1303(5)	283(4)	5740(3)
C(b25)	1691(4)	1142(4)	5431(3)
N(c11)	3056(3)	1170(3)	261(2)
N(c1)	1747(3)	1489(3)	1422(2)
N(c2)	1473(3)	2056(2)	3540(2)
N(c21)	2065(3)	3136(2)	4842(2)
C(c11)	2335(4)	404(3)	491(3)
C(c12)	2302(5)	−482(4)	139(3)
C(c13)	3047(6)	−591(4)	−477(3)
C(c14)	3775(5)	177(4)	−713(3)
C(c15)	3778(4)	1056(4)	−338(3)
C(c01)	1552(4)	597(3)	1148(3)
O(c1)	806(4)	−56(3)	1382(3)
C(c1)	931(3)	1741(3)	2020(2)
C(c2)	1166(4)	1338(3)	2863(2)
O(c2)	−522(3)	2300(2)	3455(2)
C(c02)	555(3)	2430(3)	3777(2)
C(c21)	895(4)	3080(3)	4524(2)
C(c22)	77(4)	3551(4)	4876(3)
C(c23)	480(5)	4122(4)	5579(3)
C(c24)	1684(5)	4194(4)	5891(3)
C(c25)	2456(4)	3691(3)	5515(3)

(continued)

TABLE IV. (continued)

	x	*y*	*z*	Occupancy
(b) The lattice water molecules including occupancy				
O(w1)	7678(3)	1022(3)	2552(2)	1.00
O(w2)	−1306(4)	−591(3)	2033(3)	1.00
O(w3)	6032(4)	−608(4)	2978(4)	1.00
O(w4)	5591(14)	−3984(7)	2685(7)	1.00
O(w5)	−1891(6)	3645(4)	2918(5)	1.00
O(w6)	−1340(12)	−2245(6)	2831(5)	1.00
O(w7)	2278(10)	−1132(5)	2420(5)	1.00
O(w8)	2824(9)	−3628(6)	2186(5)	1.00
O(w9)	−2250(8)	−3952(8)	1793(5)	1.00
O(w10)	942(22)	−2574(13)	3086(14)	0.50
O(w11)	−4523(18)	−2189(8)	2042(7)	0.50
O(w12)	46(27)	−4805(18)	2519(13)	0.50
O(w13)	−747(22)	4856(15)	1902(12)	0.50
O(w14)	3758(19)	−2059(10)	1388(8)	0.50
O(w15)	813(25)	−3217(35)	2891(18)	0.25
O(w16)	−3772(92)	−4545(77)	2434(54)	0.25

[a] e.s.d.s in parentheses.

The structure of the ligand molecule has a space group imposed centre of symmetry. The amide group adopts a *trans* configuration and the picolinamide moiety is closely planar.

In the previously reported deprotonated Cu(II) [9] and Ni(II) [10] structures the ligand acts as an N_4-planar tetradentate, but in the present determination it acts as a bis(N_2-bidentate) in bridging the two cobalt atoms. The octahedral stereochemistries of the cobalt atoms are attained by the bridging of three such ligands. This stereochemistry had been postulated for dimeric complexes with imine ligands of similar molecular geometry [11]. The symmetry of the dimer is D_3 (32) as shown in Fig. 3 and hence the molecule is chiral. The molecule represented in both Figs. 2 and 3 has the conformation Λ,Λ-*fac,fac*. This symmetry is in accord with the simple NMR spectrum obtained (Fig. 1) which is in turn consistent with the rotational order of the molecule. The Co··Co separation is 5.493(1) Å and the central amide N atoms describe a 30° skewed trigonal prism with a centroid to N distance of 2.42 Å. The molecular dimensions in the free and coordinated ligands are comparable.

TABLE V. Bond Lengths and Angles for bpenH$_2$[a]

(a) Distances (Å)[b]

N(11)–C(11)	1.338(2)	N(11)–C(15)	1.334(2)
C(11)–C(12)	1.383(2)	C(15)–C(14)	1.382(2)
C(12)–C(13)	1.385(2)	C(14)–C(13)	1.373(2)
C(11)–C(01)	1.508(2)	C(01)–N(1)	1.335(2)
C(01)–O(1)	1.230(2)	N(1)–C(1)	1.455(2)
C(1)–C(1′)	1.523(2)		
C(12)–H(12)	1.00(2)	N(1)–H(N1)	0.89(2)
C(13)–H(13)	1.00(2)	C(1)–H(1a)	0.98(2)
C(14)–H(14)	0.98(2)	C(1)–H(1b)	1.00(2)
C(15)–H(15)	0.95(2)		

(b) Angles (°)[b]

C(11)–N(11)–C(15)	116.8(1)	C(14)–C(13)–C(12)	118.7(1)
N(11)–C(15)–C(14)	123.7(1)	C(13)–C(12)–C(11)	118.5(1)
C(15)–C(14)–C(13)	118.7(1)	C(12)–C(11)–N(11)	123.5(1)
C(11)–C(01)–O(1)	120.3(1)	C(12)–C(11)–C(01)	119.0(1)
C(11)–C(01)–N(1)	115.8(1)	N(11)–C(11)–C(01)	117.5(1)
O(1)–C(01)–N(1)	123.9(1)	C(01)–N(1)–C(1)	121.2(1)
N(1)–C(1)–C(1′)	111.4(1)		
C(11)–C(12)–H(12)	121(1)	C(01)–N(1)–H(N1)	118(1)
C(13)–C(12)–H(12)	120(1)	C(1)–N(1)–H(N1)	121(1)
C(12)–C(13)–H(13)	119(1)	N(1)–C(1)–H(1a)	109(1)
C(14)–C(13)–H(13)	122(1)	N(1)–C(1)–H(16)	109(1)
C(13)–C(14)–H(14)	124(1)	C(1′)–C(1)–H(1a)	109(1)
C(15)–C(14)–H(14)	118(1)	C(1′)–C(1)–H(1b)	109(1)
C(14)–C(15)–H(15)	118(1)	H(1a)–C(1)–H(1b)	110(1)
N(11)–C(15)–H(15)	118(1)		

[a] e.s.d.s in parentheses. [b] Atoms marked with a prime are related to those at *x*, *y*, *z* by the centre of symmetry at the origin.

TABLE VI. Bond Lengths and Angles for Co$_2$(bpen)$_3$[a]

	x = a		*x* = b		*x* = c	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
(a) Distances (Å)						
Co(n)–N(xn1)	1.954(3)	1.941(3)	1.949(3)	1.946(3)	1.932(3)	1.943(3)
Co(n)–N(xn)	1.927(3)	1.928(3)	1.939(3)	1.933(3)	1.930(3)	1.941(3)
N(xn1)–C(xn1)	1.323(5)	1.339(5)	1.345(5)	1.339(6)	1.337(5)	1.347(5)
N(xn1)–C(xn5)	1.346(5)	1.333(5)	1.334(5)	1.343(5)	1.350(5)	1.337(5)
C(xn5)–C(xn4)	1.370(7)	1.377(6)	1.389(6)	1.368(7)	1.381(7)	1.380(6)
C(xn4)–C(xn3)	1.362(8)	1.361(7)	1.381(8)	1.346(8)	1.348(8)	1.377(7)
C(xn3)–C(xn2)	1.391(7)	1.377(7)	1.388(7)	1.394(7)	1.386(7)	1.388(6)
C(xn2)–C(xn1)	1.377(6)	1.372(6)	1.381(6)	1.351(6)	1.370(6)	1.374(6)
C(xn1)–C(xOn)	1.491(5)	1.490(5)	1.479(6)	1.499(6)	1.493(6)	1.497(5)
C(xOn)–O(xn)	1.253(5)	1.234(5)	1.257(5)	1.249(6)	1.243(5)	1.248(4)
C(xOn)–N(xn)	1.312(5)	1.322(5)	1.322(5)	1.296(6)	1.317(5)	1.311(5)
N(xn)–C(xn)	1.468(4)	1.458(5)	1.456(5)	1.462(5)	1.472(5)	1.467(5)
C(x1)–C(x2)	1.554(5)		1.545(5)		1.538(6)	

	n = 1	*n* = 2		*n* = 1	*n* = 2
(b) Angles (°)					
N(an1)–Co(n)–N(bn1)	95.4(1)	94.4(1)	N(an)–Co(n)–N(cn1)	176.8(1)	88.1(1)
N(an1)–Co(n)–N(bn)	177.6(1)	86.5(1)	N(an)–Co(n)–N(cn)	94.4(1)	95.4(1)
N(an1)–Co(n)–N(cn1)	94.3(1)	95.3(1)	N(bn1)–Co(n)–N(cn1)	93.2(1)	93.1(1)

(continued)

TABLE VI. *(continued)*

	$n = 1$	$n = 2$		$n = 1$	$n = 2$
N(an1)–Co(n)–N(cn)	86.4(1)	177.7(1)	N(bn1)–Co(n)–N(cn)	176.6(1)	87.1(1)
N(an)–Co(n)–N(bn1)	88.8(1)	177.4(1)	N(bn)–Co(n)–N(cn1)	87.3(1)	175.9(1)
N(an)–Co(n)–N(bn)	95.4(1)	95.7(1)	N(bn)–Co(n)–N(cn)	95.5(1)	95.5(1)

	x = a		x = b		x = c	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
N(xn1)–Co(n)–N(xn)	83.0(1)	83.2(1)	82.8(1)	83.1(1)	83.7(1)	82.8(1)
Co(n)–N(xn)–C(xn)	128.0(3)	128.1(2)	128.2(3)	127.7(3)	128.9(3)	127.6(3)
Co(n)–N(xn)–C(xOn)	115.3(3)	115.5(3)	115.5(3)	115.6(3)	114.8(3)	115.7(2)
C(xn)–N(xn)–C(xOn)	116.0(3)	115.7(3)	115.8(3)	116.3(3)	116.1(3)	115.7(3)
Co(n)–N(xn1)–C(xn1)	113.1(2)	113.3(3)	113.3(3)	112.8(3)	113.1(3)	113.8(2)
Co(n)–N(xn1)–C(xn5)	127.7(3)	127.5(3)	127.4(3)	128.6(3)	128.5(3)	127.4(3)
C(xn1)–N(xn1)–C(xn5)	119.0(4)	119.1(3)	119.3(3)	118.4(4)	118.2(4)	118.8(4)
N(xn1)–C(xn5)–C(xn4)	121.6(4)	121.5(4)	121.5(4)	121.6(5)	121.4(4)	121.3(4)
C(xn5)–C(xn4)–C(xn3)	119.8(4)	119.4(4)	119.1(4)	119.8(4)	120.0(4)	120.0(4)
C(xn4)–C(xn3)–C(xn2)	118.8(5)	119.5(4)	119.5(4)	118.9(5)	119.0(5)	118.6(4)
C(xn3)–C(xn2)–C(xn1)	118.5(5)	118.5(4)	118.0(5)	118.8(5)	118.9(5)	118.6(4)
C(xn2)–C(xn1)–N(xn1)	122.4(4)	122.1(4)	122.5(4)	122.3(4)	122.4(4)	122.6(4)
C(xn2)–C(xn1)–C(xOn)	122.9(4)	123.2(4)	122.5(4)	123.2(5)	122.9(4)	123.2(4)
N(xn1)–C(xn1)–C(xOn)	114.8(3)	114.7(3)	114.8(3)	114.5(4)	114.7(4)	114.2(3)
C(xn1)–C(xOn)–O(xn)	119.4(4)	120.0(3)	120.7(4)	119.5(4)	120.2(4)	119.2(4)
C(xn1)–C(xOn)–N(xn)	113.4(3)	113.0(3)	113.4(3)	113.6(4)	113.5(4)	113.3(3)
O(xn)–C(xOn)–N(xn)	127.2(4)	127.0(4)	125.8(4)	126.9(4)	126.4(4)	127.5(4)
N(x1)–C(x1)–C(x2)	113.9(3)		114.6(3)		113.9(3)	
N(x2)–C(x2)–C(x1)	113.5(3)		113.7(3)		114.5(3)	

[a] e.s.d.s in parentheses.

TABLE VII. Contact Distances (Å)[a]

(A) bpenH$_2$

(a) Intermolecular distances <3.5 Å

C(12)···O^{i}	3.139(2)	N(11)···C(O^{ii})	3.406(2)
C(13)···O^{i}	3.318(2)	C(14)···C(1^{ii})	3.446(2)

(b) Proposed hydrogen bonding

O···N(1^{iii})	3.070(1)	O···H(N1^{iii})	2.31(2)

(B) Co$_2$(bpen)$_3$·12H$_2$O

(a) Intermolecular distances <3.5 Å not involving water molecules

C(b14)···C(b14^{iv})	3.342(11)	O(b1)···C(c13^{v})	3.402(6)
C(b24)···O(c2^{i})	3.359(6)	C(c23)···C(c23^{vi})	3.455(11)

(b) Proposed hydrogen bonding between coordination and lattice water molecules

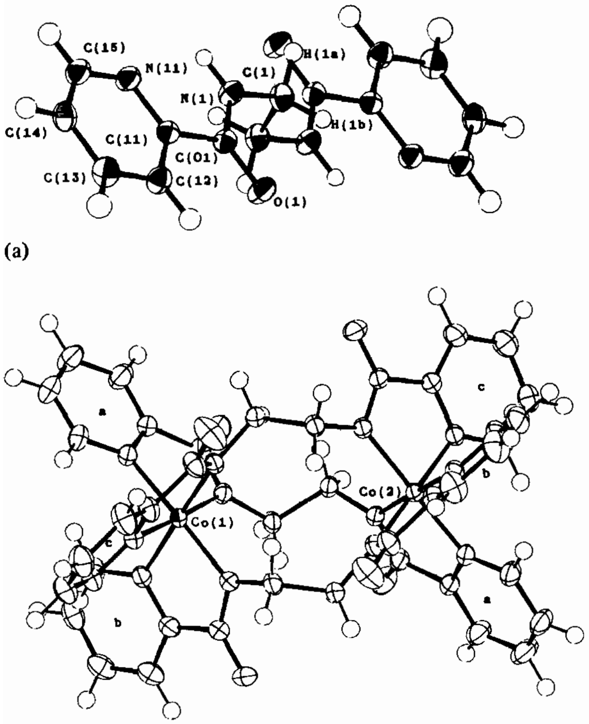
O(a1)···O(w8^{vii})	2.725(8)	O(b2)···O(w3)	2 700(6)
O(a1)···O(w12^{vii})	2.77(2)	O(b2)···O(w7)	2.837(8)
O(a1)···O(w13)	2.91(2)	O(c1)···O(w2)	2.682(5)
O(a2)···O(w4^{vii})	2.696(11)	O(c1)···O(w7)	2.911(9)
O(a2)···O(w16^{viii})	2.77(9)	O(c2)···O(w1^{x})	2.767(4)
O(b1)···O(w1)	2.764(5)	O(c2)···O(w5)	2.763(7)
O(b1)···O(w5^{ix})	2.886(7)		

[a] e.s.d.s in parentheses. Roman numeral superscripts refer to the following equivalent positions relative to atoms at x, y, z. i, $-0.5 - x, y, 0.5 - z$; ii, $- x, -y, 1 - z$; iii, $x - 0.5, -y, 0.5 - z$; iv, $1 - x, 1 - y, -z$; v, $1 - x, -y, -z$; vi, $-x, 1 - y, 1 - z$; vii, $x, 1 + y, z$; viii, $1 + x, 1 + y, z$; ix, $1 + x, y, z$; x, $x - 1, y, z$.

TABLE VIII. Data for the Anlysis of Distortions in the Free and Complexed Ligand Molecules (angles in degrees)[a]

	$bpenH_2$	$[Co_2(bpen)_3]$		
Ligand	free	a	b	c
Torsion angle				
N(1)C(1)C(2)/N(2)C(2)C(1)	180	120.2	120.8	121.5
Pyramidal distortions				
C(On)	1.1	1.0, 0.2	2.7, 0.4	0.2, 0.1
N(n)	2.1	9.5, 9.8	7.7, 6.1	5.7, 11.3
Pyridyl ring distortions				
γ		0.8, 1.7	0.4 1.7	0.1, 1.9
δ		0.4, 1.0	0.2, 1.0	0.1, 1.1
Torsion angles and specific distortions about the 'peptide unit'				
$\Delta\Psi_{CC}$	0.8	−6.2, −5.8	0.8, −2.6	−1.9, −0.2
$\Delta\omega$	2.9	−5.0, −4.7	−6.8, −6.3	−5.0, −6.0
θ_N	2.1	8.7, 8.9	7.0, 5.1	5.1, 10.4
θ_C	1.1	−1.0, 0.2	−2.7, 0.4	−0.2, −0.1
$\Delta\phi_{NC}$	94.3	−107.0, −106.9	−109.3, −109.2	−108.9, −105.5

[a]Detailed definitions of distortions and torsion angles are given in Fig. 3 and Table VI of ref. 12.



(a)

(b)

Fig. 2. Perspective drawings of (a) $bpenH_2$ and (b) $[Co_2(bpen)_3]$ molecules with thermal ellipsoids drawn to include 35% probability. The atom labelling scheme is shown in detail for the free ligand. For the complex each ligand molecule is indicated by the appropriate letter. The labelling scheme for individual atoms of each ligand is similar to that of the free ligand but with the second picolinamide moiety, coordinated to Co(2), having 2 as its first designation numeral.

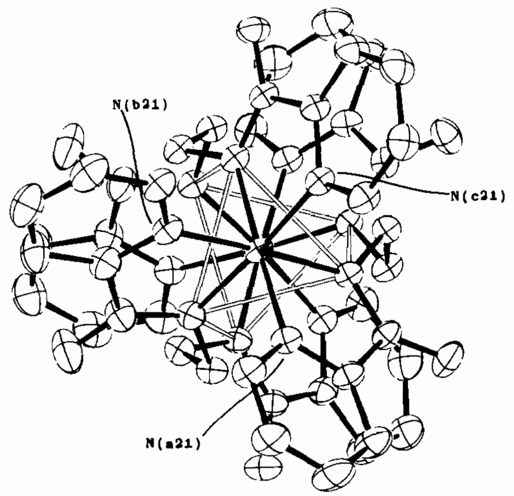


Fig. 3. A drawing of the Λ,Λ-$[Co_2(bpen)_3]$ molecule viewed down the C_3 axis. The open lines define the central skewed trigonal prism described by the six amide N atoms.

Table VIII gives details of the analysis of distortions in the free and complexed ligand molecules. This analysis shows that on coordination the ligand molecules are not unduly strained, the largest obvious effect being a 10–19% pyramidal distortion at the amide N atoms. Clearly the presence of the 5,5′-pyridyl interaction [12], a necessity for N_4-planar coordination, is not the sole determinant of such distortions. Amide group non-planarity has been observed in many other ligand systems and has been recently reviewed [13]. For the non-deprotonated complexes of the type $[M_2(bpenH_2)_3]^{4+}$ (M = divalent Mn, Fe, Co, Ni, Zn) coordination via the amide oxygen atoms rather than the nitrogens has been proposed [2]. The present structure would support this possibility since it shows that such an arrangement could be obtained by the adoption of an anti-configuration about the CH_2-CH_2 bridging unit.

Supplementary Material

Lists of observed and calculated structure factors and Tables of hydrogen atom parameters for $Co_2(bpen)_3$, of thermal parameters and of least-squares planes and their equations are available from the authors on request.

Acknowledgements

We thank Mr D. C. Craig of the School of Chemistry, University of New South Wales for the collection of intensity data for the ligand and Professor W. Robinson of the Department of Chemistry, University of Canterbury, N.Z. for the collection of intensity data for the complex.

References

1 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 120,* 165 (1986).

2 D. J. Barnes, R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 155 (1981).

3 M. W. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 53,* L91 (1981); *63,* 197 (1982).

4 R. L. Chapman and R. S. Vagg, *Inorg. Chim. Acta, 33,* 227 (1979).

5 P. Main, 'MULTAN80', Department of Physics, University of York, York, U.K.

6 G. M. Sheldrick, 'SHELXTL User Manual', Revision 3, Nicolet XRD Corporation, Cupertino, California, 1981.

7 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974, pp. 72–79.

8 C. K. Johnson, 'ORTEP', *Report ORNL-3794 (1965),* Revised 1971, Oak Ridge National Laboratory, Tenn., U.S.A., 1971.

9 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Acta Crystallogr., Sect. B, 37,* 75 (1981).

10 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 57,* 9 (1982).

11 W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc., 82,* 4834 (1960); C. M. Harris and E. D. McKenzie, *J. Chem. Soc. A,* 746 (1969).

12 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 169 (1981).

13 T. J. Collins, R. J. Coots, T. T. Furutani, J. T. Keech, G. J. Peake and B. D. Santarsiero, *J. Am. Chem. Soc., 108,* 5333 (1986).