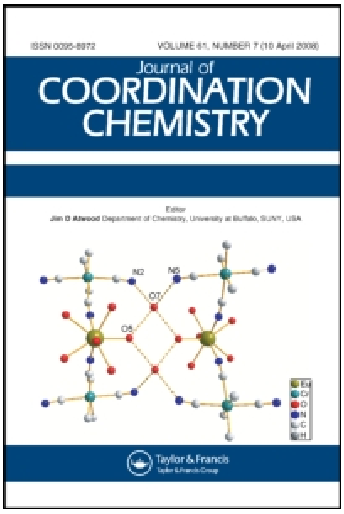

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SYNTHESIS AND STRUCTURES OF *TRIS*(PYRAZOLYL)HYDROBORATO COMPLEXES AND THEIR RELEVANCE TO CARBONIC ANHYDRASE

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A series of *tris*(pyrazolyl)hydroborato metal complexes [η^3-HB(3-R^1-5-R^2 pz)$_3$]MX (R^1 = Ph, 2′-thienyl, R^2 = CH$_3$, Ph; M = Ni, Cu, Zn, Cd; X = Cl$^-$, NO$_3^-$, CH$_3$COO$^-$), and [η^3-HB(3-Ph-5-Mepz)$_3$](3-Me-5-Phpz)Cu(PhCOO) (**8**) have been synthesized and characterized. Among them, the complexes [η^3-HB(3,5-Ph$_2$ pz)$_3$]NiCl (**3**), [η^3-HB(3-Ph-5-Mepz)$_3$]Cd(NO$_3$)(THF) (**4**), and (**8**) were analyzed by X-ray structure methods, which revealed the bidentate coordination of NO$_3^-$ in complex **4**, and isomerized ligands in complex **8**. As model compounds of carbonic anhydrase (CA), all of these structures were contrasted to that of the active site of CA; the chloride may be the closest model compound among them. The relationship between the coordination modes of NO$_3^-$, CH$_3$COO$^-$, and PhCOO$^-$ in the complexes and their IR spectra is also discussed.

Keywords: X-ray structures; *tris*(pyrazolyl)hydroborato; complexes; carbonic anhydrase

INTRODUCTION

The *tris*(pyrazolyl)hydroborato ligand [HB(pz)$_3$]$^-$ has played an important role in modeling metalloenzyme active sites since 1980. Its metal complexes have been employed in the study of carbonic anhydrase (CA), haemocyanin, tyrosinase, non-heme iron proteins, and the polymanganese site of the

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photo-system II oxygen-evolving centre.[1-5] The active site structure of CA has two key features: one is a four-coordinated distorted tetrahedral zinc centre and the other is the unidentate coordination mode of the bicarbonate binding to zinc, which acts as an important intermediate in the reaction[6] $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$. When bulky substituents, *e.g.*, *t*-Bu, Ph and isopropyl are at the 3-position of the pyrazole ring of $[HB(pz)_3]^-$, which prevents the binding of a second equally hindered terdentate ligand, a four-coordinate complex is generally formed with a single axial ligand.[1,7] Since the unidentate bicarbonate zinc complex is a significant intermediate in the catalytic reaction of CA, it will be of interest to investigate the analogues of it. Unfortunately, most early transition metal complexes of bicarbonate are unstable. Therefore, our recent work has centred on studying a series of anionic ($X = Cl^-$, NO_3^-, CH_3COO^-, $PhCOO^-$) derivatives of some metals $[HB(pz)_3]MX$, on the basis that structural changes would indicate the relative tendencies of different metal centres to support unidentate *versus* bidentate coordination for X. In this paper, we describe the synthesis and structures of some anion (Cl^-, NO_3^-, CH_3COO^-, $PhCOO^-$) derivatives of certain metals that are supported by *tris*(pyrazolyl)hydroborato ligation (Scheme I). In particular, in terms of CA, the coordination modes of X ($X = NO_3^-$, CH_3COO^-, $PhCOO^-$) in the complexes will be of central importance.

EXPERIMENTAL

Materials and Physical Measurements

All reagents were A.R. grade and used without further purification. ^1H NMR spectra (δ, ppm) were recorded on a Bruker AM-400A spectrometer; IR spectra were obtained from KBr disks using a Nicolet-10DX FT-IR instrument and are reported in cm^{-1}. Elemental analyses were obtained by using a Vario EL elemental analyzer.

The terdentate ligands $K[BH(3\text{-}R^1\text{-}5\text{-}R^2\text{-}pz)_3]$ ($R^1 = Ph$, 2′-thienyl, $R^2 = Ph$, CH_3), were prepared and characterized as previously described.[8]

Preparation of the Complexes

To a solution of $K[BH(3\text{-}R^1\text{-}5\text{-}R^2\text{-}pz)_3]$ (2 mmol) in THF (10 cm^3) was added a solution of metal salt (2.3 mmol) in THF (20 cm^3) and the mixture was stirred at room temperature for 12 h and filtered. The solvent was

a. $K[BH(3\text{-}R^1\text{-}5\text{-}R^2\text{-}pz)_3] \xrightarrow[RT]{MX_2} [\eta^3\text{-}HB(3\text{-}R^1\text{-}5\text{-}R^2\text{-}pz)_3]MX$

R^1=Ph, R^2=CH_3, M=Cu, X=Cl, **1**

R^1=2′-thie, R^2=CH_3, M=Cu, X=Cl, **2**

R^1=R^2=Ph, M=Ni, X=Cl, **3**

R^1=Ph, R^2=CH_3, M=Cd, X=NO_3, **4**

R^1=R^2=Ph, M=Zn, X=CH_3COO, **5**

R^1=Ph, R^2=2′-thie, M=Ni; X=NO_3, **6**

R^1=Ph, R^2=2′-thie, M=Zn, X=CH_3COO, **7**

b. $K[BH(3\text{-}Ph\text{-}5\text{-}Mepz)_3]$ + 3(5)-Ph-5(3)-Mepz + Cu

$\xrightarrow{(PhCOO)_2} [\eta^3\text{-}HB(3\text{-}Ph\text{-}5\text{-}Mepz)_3](3\text{-}Me\text{-}5\text{-}Phpz)Cu(PhCOO)$ **8**

SCHEME I

removed from the filtrate under reduced pressure and the residue obtained washed with hexane, crystallized from appropriate solvents (see below), and isolated by filtration, washed and dried *in vacuo*. Physical properties and elemental analyses of the complexes **1**–**8** are listed in Table I.

1: (CH_3COCH_3); IR: 2540($\nu_{B\text{-}H}$), 1365(δ_{CH3}), 759($\gamma_{=CH}$ of Ph), 692(δ_{ring} of Ph); ^1H NMR ($CDCl_3$): 7.65–7.21(m, 15H, Ph), 6.22(s, 3H, pz), 2.62(s, 9H, CH_3).

2: (CH_3Ph/CH_3COCH_3); IR: 2528(ν_{B-H}), 1371(δ_{CH3}), 854, 697(thienyl); ^1H NMR (CD_3CN): 7.92(m, 3H, αH of thienyl), 7.50–7.36(m, 5H, Ph of CH_3Ph), 7.23(m, 6H, βH of thienyl), 6.26(s, 3H, pz), 2.66(s, 9H, 5-CH_3), 2.33(s, 3H, CH_3 of CH_3Ph).

3: [CH_2Cl_2/CH_3CN(2 : 1)]; IR: 2612(ν_{B-H}), 758($\gamma_{=CH}$ of Ph), 694(δ_{ring} of Ph); ^1H NMR(DMSO): 7.57(m, 12H, ortho H of Ph), 6.97(m, 18H, *meta*, *para* H of Ph), 6.48(s, 3H, pz).

4: (Pentane/THF); IR: 2546(ν_{B-H}), 1495[$\nu_a(NO_2)$], 1265($\nu_{N=O}$), 1028[$\nu_s(NO_2)$]; ^1H NMR ($CDCl_3$): 7.50(m, 6H, *ortho* H of Ph), 7.22 (m, 9H, *meta*, *para* H of Ph), 6.21(s, 3H, pz), 3.64(m, 4H, αH of THF), 2.56(s, 9H,CH_3), 1.76(m, 4H, βH of THF).

TABLE I Physical properties and elemental analyses for the complexes

No.	*Colour*	*Yield*(%)	*M.p.*(°C)	*Found% (Calcd. values %)*			
				C	*H*	*N*	*S*
1	Dark green	34.7	221–222	62.04	4.76	14.35	
				(61.87)	(4.81)	(14.44)	
2	Yellow green	26.8	152–153	53.78	4.16	12.28	13.92
				(53.76)	(4.33)	(12.14)	(13.90)
3	Pale purple	28.6	> 350	70.57	4.38	11.23	
				(70.78)	(4.46)	(11.01)	
4	Colourless	39.8	224–225(dec.)	56.03	4.87	13.39	
				(55.90)	(4.93)	(13.43)	
5	Colourless	74.2	174–176(subl.)	70.93	4.48	10.67	
				(71.10)	(4.66)	(10.59)	
6	Pale green	46.2	> 350	57.69	3.39	12.08	12.13
				(57.94)	(3.47)	(12.13)	(11.91)
7	Colourless	40.8	302–303	60.74	3.67	10.41	11.72
				(60.63)	(3.82)	(10.35)	(11.86)
8	Green	36.2	215–216	68.27	5.11	12.87	
				(68.35)	(5.23)	(13.02)	

5: [CH_3CN/CH_2Cl_2 (3 : 2)]; IR: 2650(ν_{B-H}), 1550($\nu_{C=O}$), 1466(ν_{C-O}), 758($\gamma_{=CH}$ of Ph), 694(δ_{ring} of Ph); ^1H NMR ($CDCl_3$): 7.68(m, 12H, *ortho* H of Ph), 7.01(m, 18H, *meta*, *para* H of Ph), 6.48 (s, 3H, pz), 1.62(s, 3H, CH_3COO).

6: [THF/EtOH(1:1)]; IR: 2631(ν_{B-H}), 1486[$\nu_a(NO_2)$], 1281[$\nu_{(N=O)}$], 1010[$\nu_s(NO_2)$]; ^1H NMR ($CDCl_3$): 7.62(m, 6H, ortho H of Ph), 7.44–7.09(m, 12H, *meta*, *para* H of Ph and αH of thienyl), 6.96(m, 6H, βH of thienyl), 6.43(s, 3H, pz).

7: [CH_3CN/CH_2Cl_2(1 : 1)]; IR: 2630(ν_{B-H}), 1569($\nu_{C=O}$), 1449(ν_{C-O}), 764($\gamma_{=C-H}$ of Ph), 696(δ_{ring} of Ph); ^1H NMR($CDCl_3$): 7.63(m, 6H, *ortho* H of Ph), 7.45–7.11(m, 12H, *meta*, *para* H of Ph andαH of thienyl), 6.98(m, 6H, βH of thienyl), 6.44(s, 3H, pz), 1.65(s, 3H, CH_3COO).

8: At room temperature, equal amounts (20 mmol) of copper powder (0.32 g), dibenzoyl peroxide (1.21 g), 3(5)-phenyl-5(3)-methylpyrazole (0.79 g) and its hydroborato derivative (2.60 g), were mixed with 200 cm^3 of acetone and stirred for 30 h. Green solids formed were isolated by filtration, recrystallized from ethanol, filtered, washed with benzene and dried in air. IR data: 2519(ν_{B-H}), 1593($\nu_{C=O}$), 1312(ν_{C-O}), 1389(δ_s of CH_3), 764($\gamma_{=CH}$ of Ph), 694(δ_{ring} of Ph); ^1H NMR ($CDCl_3$): 8.42(m, 5H, PhCOO), 7.91(m, 8H, *ortho* H of Ph), 7.48(m, 12H, *meta*, *para* H of Ph), 6.21(s, 4H, pz), 2.59(s, 12H, CH_3).

Crystal Structure Determination

Data collection was performed with MoKα radiation ($\lambda = 0.71073$ Å) on a Siemens P4 diffractometer with data reduction using the Siemens SHELXTL program system. Experimental details for the structure determination of **3**, **4** and **8** are summarized in Table II, while Tables III and IV

TABLE II Crystal and intensity collection data for the complexes

	3	4	8
Chemical formula	$C_{45}H_{34}N_6BClNi$	$C_{34}H_{36}N_7BO_4Cd$	$C_{49}H_{45}N_8BO_{2.5}Cu$
Formula weight	762.9	729.9	860.3
Crystal size (mm)	0.56 × 0.50 × 0.40	0.60 × 0.46 × 0.40	0.58 × 0.46 × 0.46
Lattice	Rhombohedral	Triclinic	Triclinic
Space group	$R3$	$P\bar{1}$	$P\bar{1}$
Cell constants			
a (Å)	12.9120(12)	11.3030(10)	12.722(2)
b (Å)	12.9120(12)	12.099(2)	13.068(2)
c (Å)	19.323(3)	12.607(2)	15.857(3)
α, deg.	90	102.050(10)	68.090(10)
β, deg.	90	91.780(10)	74.140(10)
γ, deg.	120	93.620(10)	80.370(10)
V (Å^3)	2790.0(6)	1681.0(4)	2346.4(7)
Z	9	2	2
Dc (g cm^{-3})	1.364	1.442	1.218
μ (mm^{-1})	0.636	0.698	0.513
2θ range, deg.	4.2–52.0	3.3–48.0	3.86–50.0
No. of data	1318	5229	8060
No. of parameters	210	544	680
Goodness of fit on F^2	0.990	1.067	0.914
R	0.0270	0.0302	0.0459
R_w (unitweights)	0.0580	0.0805	0.1152

TABLE III Selected bondlengths (Å) for the complexes

3		4		8			
Ni–Cl	2.200(2)	Cd–O(1)	2.334(3)	Cu–O(1)	1.968(2)	N(7)–N(8)	1.360(3)
Ni–N(2)	2.038(2)	Cd–O(2)	2.356(3)	Cu–N(2)	2.030(3)	N(8)–C(34)	1.334(4)
N(1)–C(7)	1.359(4)	Cd–N(1)	2.282(3)	Cu–N(4)	2.266(3)	C(4)–C(5)	1.476(4)
N(1)–N(2)	1.369(3)	Cd–N(3)	2.316(3)	Cu–N(6)	2.028(3)	C(41)–O(1)	1.267(4)
N(1)–B	1.544(3)	Cd–N(5)	2.300(3)	Cu–N(7)	2.016(3)	C(41)–O(2)	1.254(4)
N(2)–C(9)	1.350(4)	N(7)–O(3)	1.218(4)	N(1)–C(2)	1.345(4)	C(33)–C(34)	1.385(5)
C(6)–C(7)	1.475(4)	N(7)–O(1)	1.266(5)	B–N(1)	1.544(4)	C(32)–C(33)	1.393(5)
C(7)–C(8)	1.380(5)	N(7)–O(2)	1.236(5)	B–N(3)	1.526(5)	N(7)–C(32)	1.344(4)
C(8)–C(9)	1.392(5)	B–N(2)	1.550(5)	B–N(5)	1.548(5)	N(2)–C(4)	1.332(4)
C(9)–C(10)	1.475(4)	B–N(4)	1.541(5)	N(1)–N(2)	1.379(3)	C(3)–C(4)	1.400(5)
		B–N(6)	1.553(5)	C(1)–C(2)	1.501(4)	C(2)–C(3)	1.364(5)
		Cd–O(4)	2.391(2)	N(3)–C(12)	1.359(4)	N(5)–C(22)	1.353(4)

TABLE IV Selected bond angles (°) for the complexes

3		4		8	
N(2)–Ni–Cl	123.20(7)	O(1)–Cd–O(2)	53.78(12)	O(1)–Cu–N(7)	95.83(10)
N(2A)–Ni–Cl	123.20(7)	Cd–O(1)–N(7)	95.2(3)	O(1)–Cu–N(6)	161.79(10)
N(2B)–Ni–Cl	123.20(7)	Cd–O(2)–N(7)	95.0(3)	N(7)–Cu–N(6)	89.64(10)
N(2A)–Ni–N(2)	92.88(9)	N(1)–Cd–O(1)	162.38(12)	O(1)–Cu–N(2)	89.12(9)
N(2A)–Ni–N(2B)	92.88(9)	N(3)–Cd–O(1)	102.96(11)	N(7)–Cu–N(2)	173.89(11)
N(2B)–Ni–N(2)	92.88(9)	N(5)–Cd–O(1)	106.71(12)	N(6)–Cu–N(2)	84.57(10)
C(7)–N(1)–N(2)	109.8(2)	N(1)–Cd–O(2)	109.46(11)	O(1)–Cu–N(4)	102.30(9)
C(7)–N(1)–B	128.0(3)	N(1)–Cd–O(4)	84.11(9)	N(7)–Cu–N(4)	93.84(10)
N(2)–N(1)–B	120.0(3)	N(3)–Cd–O(4)	167.09(9)	N(6)–Cu–N(4)	94.62(10)
C(9)–N(2)–N(1)	107.0(2)	N(5)–Cd–O(4)	91.22(9)	N(2)–Cu–N(4)	88.59(10)
C(9)–N(2)–Ni	141.3(2)	O(1)–Cd–O(4)	89.91(11)	C(41)–O(1)–Cu	132.9(2)
N(1)–N(2)–Ni	111.8(2)	O(2)–Cd–O(4)	89.56(11)	N(2)–N(1)–B	121.1(2)
N(1A)–B–N(1B)	108.9(2)	N(2)–B–N(4)	109.5(3)	C(4)–N(2)–N(1)	106.6(2)
N(1A)–B–N(1)	108.9(2)	N(2)–B–N(6)	111.2(3)	C(4)–N(2)–Cu	138.0(2)
N(1B)–B–N(1)	107.4(3)	N(3)–Cd–O(2)	97.16(11)	N(4)–N(3)–B	119.6(2)
C(7)–C(8)–C–(9)	106.7(3)	N(5)–Cd–O(2)	160.48(12)	C(14)–N(4)–Cu	139.3(2)
N(2)–C(9)–C(8)	109.2(3)	N(1)–Cd–N(3)	83.26(10)	N(3)–N(4)–Cu	111.5(2)
N(1)–C(7)–C(6)	123.0(3)	N(1)–Cd–N(5)	90.01(9)	C(22)–N(5)–B	131.0(3)
C(6)–C(7) –C(8)	129.6(3)	N(3)–Cd–N(5)	86.12(9)	N(6)–N(5)–B	119.4(2)
		O(3)–N(7)–O(1)	119.7(5)	C(24)–N(6)–Cu	135.7(2)
		O(3)–N(7)–O(2)	124.3(5)	N(5)–N(6)–Cu	116.2(2)
		O(1)–N(7)–O(2)	116.0(3)	N(8)–N(7)–Cu	118.3(2)
				N(3)–B–N(1)	110.6(3)
				N(3)–B–N(5)	110.1(3)
				N(5)–B–N(1)	107.9(3)

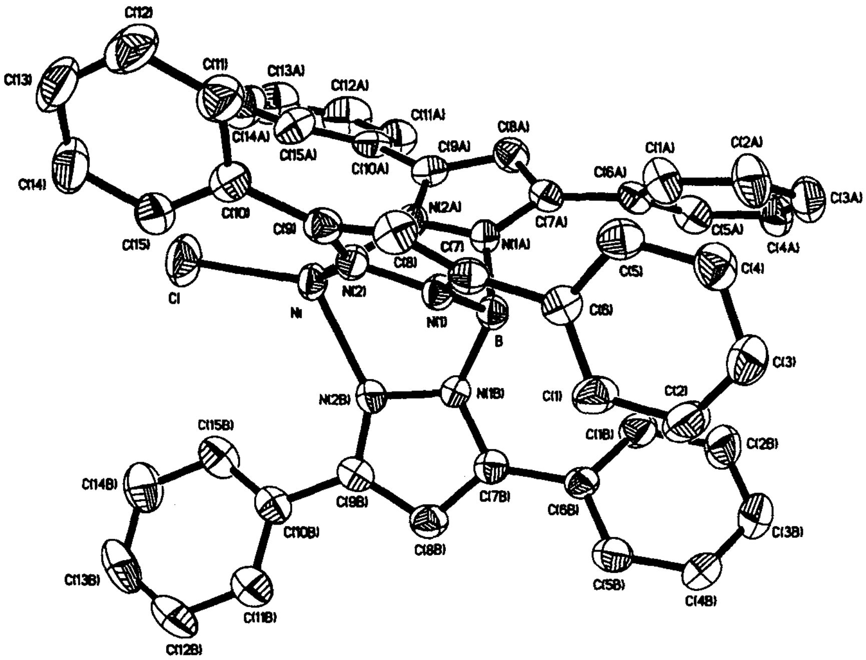


FIGURE 1a The molecular structure of complex 3.

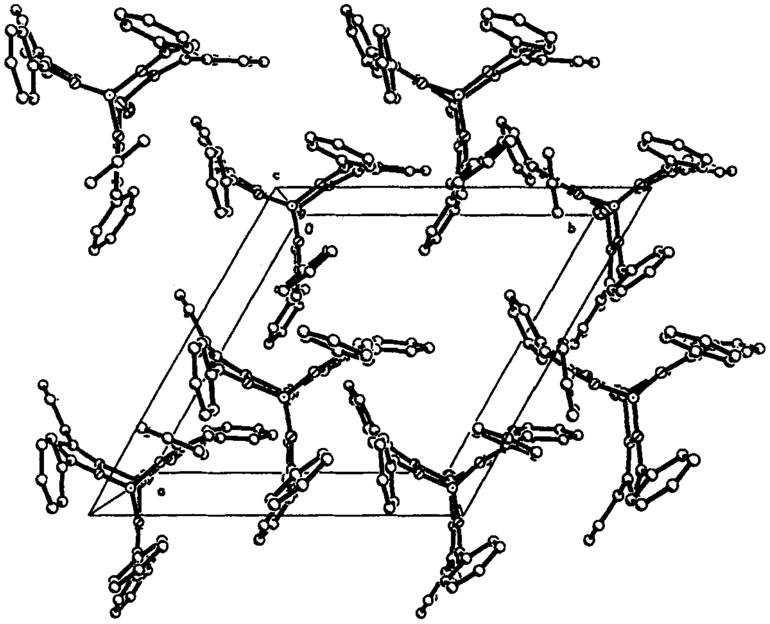


FIGURE 1b Crystal packing in the unit cell for complex 3.

give a listing of selected bondlengths and angles respectively. Perspective views of **3**, **4** and **8** are presented in Figures 1a–3a, and diagrams of crystal packing in the unit cell for each of them are given in Figures 1b–3b.

RESULTS AND DISCUSSION

IR Spectra

From the IR spectra of the complexes, we could find characteristic vibration peaks of BH, Me, Ph, thienyl and pyrazolyl groups, and we may also assign certain peaks to stretching vibrations of coordinated NO_3^-, CH_3COO^-, and $PhCOO^-$. According to Nakamoto,[10] there is a close relation between the coordination mode of X^- and its IR spectrum (see Tables V and VI). Nakamoto suggested that in a series of structurally similar complexes the greater the difference between the highest frequency peak and the second, the greater the tendency of bidentate coordination of NO_3^- to the metal. Since the structure of **4** had been verified by an X-ray crystal structure determination and nitrate in it is bidentate, based on the Table V, we

TABLE V IR data for nitrate in its complexes

Complex	*$^*p_1$*	*p_2*	*$p_1 - p_2$*	*Coord. mode*	*Ref.*
4	$1495[\nu_a(NO_2)]$	$1265(\nu_{N=O})$	230	bidentate	
6	$1486[\nu_a(NO_2)]$	$1281(\nu_{N=O})$	205	bidentate	
$LNi(NO_3)$	$1523[\nu_a(NO_2)]$	$1279(\nu_{N=O})$	244	bidentate	8
$LCu(NO_3)$	$1479[\nu_a(NO_2)]$	$1267(\nu_{N=O})$	212	bidentate	8
$LZn(NO_3)$	$1460[\nu_a(NO_2)]$	$1286(\nu_{N=O})$	174	anisobidentate	8
$[Ni(en)_2(NO_3)_2]$	$1420[\nu_a(NO_2)]$	$1305[\nu_s(NO_2)]$	115	unidentate	10

*Here, P_1 denotes the highest frequency peak of NO_3 and p_2 the second; L = [η^3-HB{3-(2′-thie)-5-Mepz}$_3$].

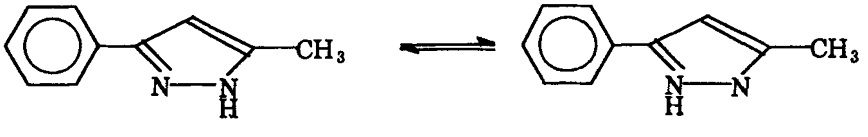
TABLE VI Relationship between the coordination mode of acetate or benzoxy groups and their IR spectra

Compound	$\nu_{C=O}$	$\nu_{C\text{-}O}$	$\nu_{C=O} - \nu_{C-O}$	*Mode*	*Ref.*
CH_3COO^- (ac)	1560	1416	144		
$Ru(ac)_2(CO)_2(PPh_3)_2$	1613	1315	298	Unidentate	9
8	1593	1312	281	Unidentate	
$[Pd(ac)_2(PPh_3)]_2$	1629	1314	315	Unidentate	11
	1580	1411	169	Bridged biDentate	
$Rh_2(ac)_2(CO)_3(PPh_3)$	1580	1440	140	Bridged biDentate	15
$RuH(ac)(PPh_3)_2$	1526	1449	77	Bidentate	9
5	1550	1466	84	Bidentate	
7	1569	1449	120	Bidentate	
[η^3-HB(3,5-$Pr^i{}_2$pz)$_3$]-Cu(m-ClC_6H_4COO)	1515	1440	75	Bidentate	16

may deduce that in complex **6** it may be also bidentate. The results from Table VI, for [$\nu_{(C=O)} - \nu_{(C-O)}$] suggesting the bridged carboxylate was somewhere between unidentate and bidentate are also in accord with his conclusions.

Ligand Isomerization

Bondlength data [N(7)–C(32) = 1.344(4) Å, N(8)–C(34) = 1.334(4) Å], could not distinguish which N atom is the 1-position of the pyrazole ring formed by N(7), N(8) and the other three carbon atoms. However, there is a hydrogen atom binding to N(8). Therefore, this ligand would be 3-methyl-5-phenylpyrazole, an isomer of 3-phenyl-5-methylpyrazole in another ligand [η^3-HB(3-Ph-5-Mepz)$_3$]. Pyrazole derivatives are at equilibrium in solution and melt state; when reacted with KBH_4 isomer I is preferentially attacked and finally forms K[HB(3-Ph-5-Mepz)$_3$], whereas II has a great steric predominance during the formation of the complex, as two adjacent Ph groups [at C(24), C(32)] must interact somewhat. Steric effects have great influence on the formation of the complex. We found this phenomenon in previous work.[8]



I II

Molecular Structure

The molecular structures of the complexes [η^3-HB(3,5-ph$_2$pz)$_3$]NiCl, [η^3-HB(3-ph-5-Mepz)$_3$]Cd(NO$_3$)(THF), and [η^3-HB(3-Ph-5-Mepz)$_3$](3-Me-5-Phpz)Cu(PhCOO) are illustrated in Figures 1–3. Each of the complexes exhibits a slightly different coordination of the *tris*(pyrazolyl)hydroborato ligands to the metal centre; the average M–N bondlengths and N–M–N angles changes across the series Ni, Cu, Cd: [2.038 Å, 92.88°], [2.108 Å, 89.26°], [2.299 Å, 86.46°], a reflection of the covalent radius of the metal (Ni < Cu < Cd). Moreover the Cd–N bond length is shorter than those in the six coordinate sandwich complex [η^3-HB(3,5-Me$_2$pz)$_3$]$_2$Cd[2.36(1) and 2.43(2) Å].[12]

Complex **3**, has a C_3 axis, the nickel atom is coordinated by three nitrogen atoms and one chlorine atom and the configuration of the complex is a trigonally distorted tetrahedron, as evidenced by the three small N–Ni–N [92.88(9)°] bond angles, and three large N–Ni–Cl [123.20(7)°] bond angles. The bondlength Ni–Cl [2.200(2) Å] is comparable to Zn–Br [2.280(1) Å] in complex [η^3-HB(3-Phpz)$_3$]ZnBr,[13] but significantly shorter than M–I [2.511(3) and 2.673(2) Å] in complexes [η^3-HB(3,4-Ph$_2$-5-Mepz)$_3$]CoI·C_7H_8[7] and [η^3-HB(3-Bu^{t}pz)$_3$]Cd I;[1] this must be attributed to the large size of I compared to its lighter congeners Br and Cl. The coordination environment of **3** also compares reasonably well with a theoretical calculation for the active site of CA, with bondlengths and angles of Zn–O (1.96 Å), Zn–N (2.10 Å), and O–Zn–N (117.6°).[14] Considering the ligands of complex **1** and **2** are very similar to those of the Ni analogue, we may deduce that both **1** and **2** must have a very close structure to **3**, *i.e.*, distorted tetrahedral.

The coordination mode of nitrate in complex **4** is bidentate [2.334(3) and 2.356(3) Å], which is close to that [2.272(6) and 2.295(7) Å] of $[\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3]\text{Cd(NO}_3)$,[1] but different from previous observed values in $[\eta^3\text{-HB\{3-(2'-thie)-5-Mepz\}}_3]\text{Zn(NO}_3)$,[8] *i.e.*, 1.966(4) and 2.463(4) Å. Obviously, the different coordination mode of nitrate results from the different metal centre.

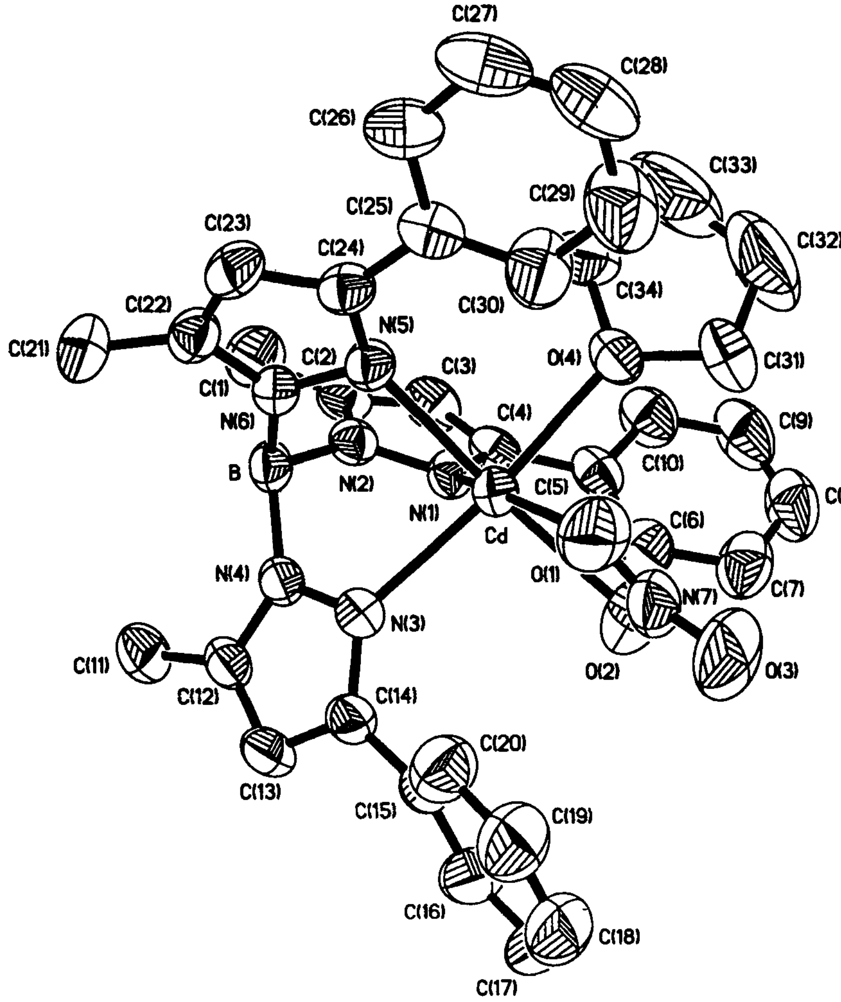


FIGURE 2a The molecular structure of complex **4**.

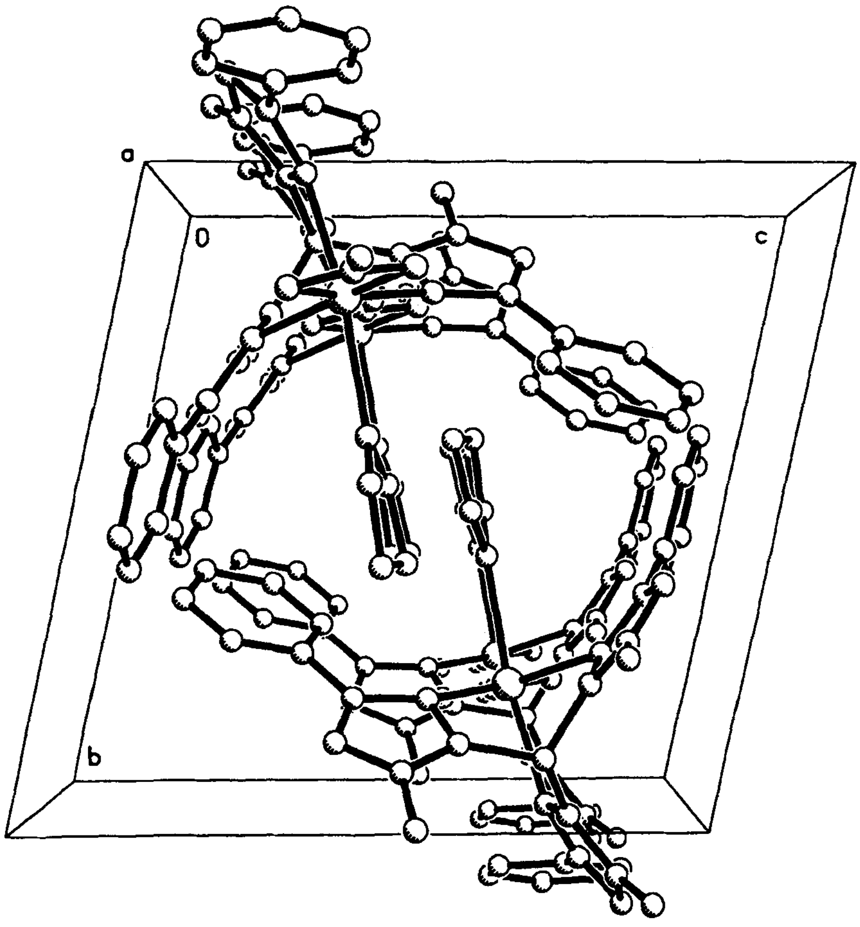


FIGURE 2b Unit cell pacing diagram for complex 4.

As illustrated in Figure 3, the copper atom is coordinated by four nitrogen atoms and one oxygen atom, the coordination environment around copper being a distorted square pyramid with N(4) at the apical position. The coordination mode of benzoxy in complex **8** is unidentate, with Cu–O(1) being 1.968(2) Å, slightly shorter than 2.043(7) and 2.013(8) Å of bidentate coordinated *m*-chlorobenzoxy in $[\eta^3\text{-HB}(3,5\text{-Pr}^i{}_2\text{pz})_3]\text{Cu-(m-Cl-}C_6H_4\text{COO)}$.[16]

Since the coordination mode of nitrate and acetate in **4–7** is bidentate, benzoxy exhibits unidentate coordination in complex **8** but has four coordinated N atoms. Therefore, the coordination number of complexes **4–8** is

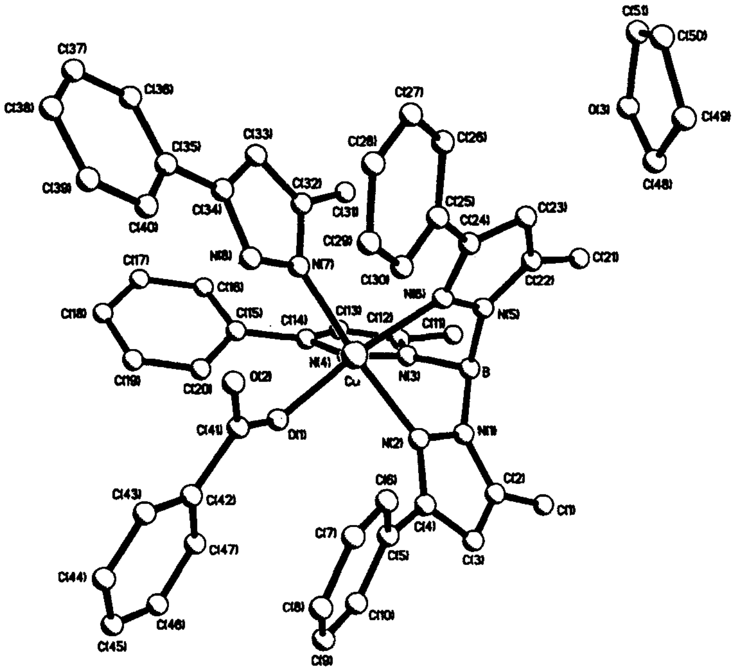


FIGURE 3a ORTEP diagram of **8**.

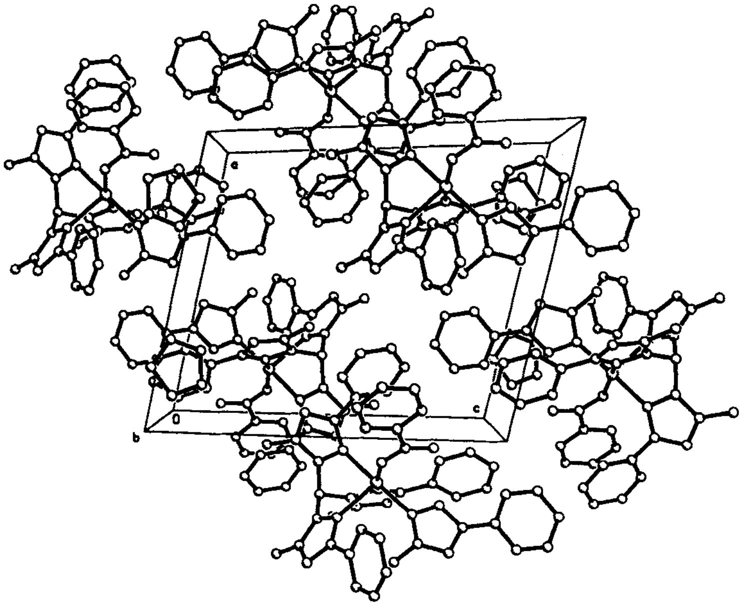


FIGURE 3b Unit cell packing diagram for **8**.

five or six. Only the chloride species **1–3** are structurally model compounds of CA.

Supplementary Data

Full lists of data for the three structures are available from the authors upon request.

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