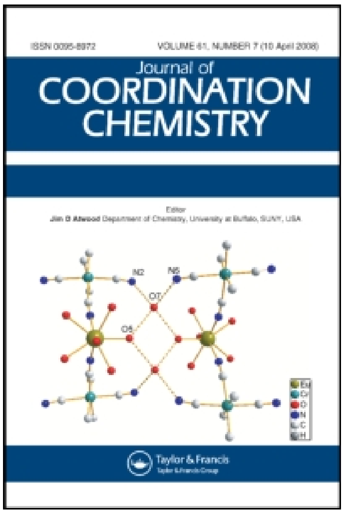

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PHOTOCHEMICAL ACTIVATION OF CARBON DIOXIDE BY VISIBLE LIGHT MEDIATED BY COBALT(II) AND NICKEL(II) COMPLEXES OF 1, 6-BIS(BENZIMIDAZOL-2-YL)-2, 5-DITHIAHEXANE (BBDH)

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Reactions between crystalline $Ni(NO_3)_2$ or $Co(ClO_4)_2$ $6H_2O$ and 1,6-*bis*(benzimidazol-2-yl)-2, 5-dithiahexane (BBDH) in ethanol afford the insolubles $[Ni(BBDH)(H_2O)_2](NO_3)_2$ or $[Co(BBDH)(H_2O)_2](ClO_4)_2$ and coloured solutions. The action of CO_2 and visible light on these suspensions at room temperature yields new nickel(II) or cobalt(II) 2- carboxylato benzimidazolates, $[O_2C\text{-}BzIm]^{2-}$, of formula $[Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](NO_3)_2$ (**I**) and $[Co_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)]$ $(ClO_4)_2$ (**II**), respectively. The crystal and molecular structure of **I** and **II** have been elucidated by single crystal X-ray analysis. The complex **I** crystallizes in the monoclinic space group *C2/c*, with a = 15.371(3), b = 13.393(3), c = 22.790 (4) Å, and β = 99.54(4)°. The unit cell comprises four formula units with half the binuclear cation complex in the asymmetric unit. The $[O_2C\text{-}BzIm]^{2-}$ bridges two distorted octahedral nickel(II) ions having a Ni—Ni distance of 5.397(2) Å. Complex **II** crystallizes in the triclinic space group $P1$, with cell data a = 13.351(5), b = 18.960(5), c = 11.379(3) Å, α = 91.14(2), β = 107.93(3), and γ = 100.88(3)°. The cation complex consist of a dimeric unit with two distorted octahedral cobalt(II) ions being bridged by a 2-carboxylatobenzimidazolato anion with a Co—Co distance of 5.285(6) Å. IR spectra are reported. A plausible mechanism by which complexes **I** and **II** are formed is also reported.

Keywords: Crystal structure; nickel(II); cobalt(II); 2-carboxylatobenzimidazolato; carbon dioxide

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INTRODUCTION

The fact that CO_2 fixation is the basic reaction by which natural photosynthesis produces organic matter has in recent years inspired increasing research on the artificial activation of CO_2. Possible applications of artificial photosynthesis include its use for recycling the products of combustion and respiration,[1–3] as a general synthetic strategy for the incorporation of CO_2 in organic molecules,[4, 5] and as a means of using CO_2 as a C_1 precursor for fuels and industrial raw materials.[6–8] The goal of research in this area — to discover processes minimizing the considerable amount of energy required for CO_2-based syntheses — can be approached by the use of metal-based catalysts.[9] In particular, work on catalysis of CO_2 activation by transition metal complexes (TMCs) has included chemical,[10–12] electrochemical[13–16] and photochemical[17–19] approaches. Surprisingly, photochemical studies have until recently been relatively few, and many of them concerned the photochemical reduction of CO_2 to CO.

As far as we know, C—C bond formation by coupling to a coordinated ligand has hitherto only been observed in the case of unsaturated hydrocarbon substrates (alkynes, alkenes, dienes, sterically strained rings and benzene), which in the presence of certain metal complexes react with CO_2 to form a product containing both a new C—C bond and the two oxygen atoms of the carbon dioxide molecule.[20] For example, certain aromatic compounds afford small yields of the corresponding aromatic acids when reacted with CO_2 in the presence of palladium(II) salts, which bring about direct activation of an aromatic C—H bond.[21] However, in this work we found that certain TMCs of 1, 6-*bis*(benzimidazol-2-yl)-2,5-dithiahexane (BBDH) yield the 2-carboxylatobenzimidazolato dianion, $[O_2C\text{-BzIm}]^{2-}$ (coordinated to the metal) when reacted with CO_2 in the presence of visible light. This is the first reported instance of the insertion of CO_2 in a metal complex by formation of a C—CO_2 bond; the carboxylated products were totally characterized by X-ray diffraction.

1H-Imidazole-2-carboxylic acids are rather rare because their synthesis has hitherto involved either construction of the imidazole ring from a precursor with the carboxyl group at what will be position 2 of the imidazole,[22] substitution of imidazole with isocyanate at high temperature,[23] or treatment of the *N*-protected imidazole with *n*-BuLi[24] followed by addition of the carboxylate anion to the electrophilic reagent. The most popular of these methods is probably the last, but even though recent developments[25] have allowed the use of gentler deprotection conditions than those required previously (which gave rise to many difficulties), a carboxyl substituent has little chance of survival. Certainly, few metallic complexes of compounds of this type are known, although 2-carboxylatoimidazole complexes with pentaamineruthenium(II/III)[26] and pentacyanoferrate(II/III)[27] have been reported. We know of no previous syntheses of metal complexes of 2-carboxilatoimidazolates. It is hoped that the reaction described in this paper may prove to be a generally applicable approach to this class of compound and, by appropriate work-up, to the corresponding unmetallated 1H-imidazole-2-carboxylic acids.

EXPERIMENTAL

Materials

BBDH was prepared by a published method.[28] Crystalline $Ni(NO_3)_2$, $Co(ClO_4)_2 \cdot 6H_2O$ and solvents were reagent grade commercial products.

Preparation of $[Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](NO_3)_2 \cdot 2H_2O \cdot 2EtOH$ (I)

A solution of 0.40 g (2.21 mmol) of crystalline $Ni(NO_3)_2$ in 10 cm^3 of ethanol was added to a suspension of 0.78 g (2.21 mmol) of freshly prepared BBDH in 50 cm^3 of the same solvent, and the mixture was stirred for 15 days. A powdery solid product was separated by filtration (*Anal:* calcd. for $Ni(BBDH)(NO_3)_2 \cdot 2EtOH$: C, 42.0; H, 4.55; N, 13.36%. Found: C, 42.2; H, 3.85; N, 14.11%). Slow concentration of the greenish filtrate in air yielded green crystals of **I**.

Anal: calcd. for $[Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](NO_3)_2 \cdot 2H_2O \cdot 2EtOH$:C, 46.3; H, 4.19; N, 14.10%. Found: C, 47.1; H, 4.78; N, 14.11%. Mass spectrum(*m/z*): 985 $[Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{–}BzIm)]^+$. IR($cm^1$): 3200*s, br* ν(NH), 1629*s* $\nu_{as}(COO^-)$ 1390*m* δ(NH), 1362*s* $\nu_s(COO^-)$, 1350*s* $\nu_3(NO_3^-)$, 838*m* $\nu_2(NO_3^-)$, 714*w* $\nu_4(NO_3^-)$, 690*w* ν(CS).

Preparation of $[Co_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](ClO_4)_2 \cdot 2H_2O \cdot EtOH$ (II)

A solution of 0.62 g (1.7 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ in 10 cm^3 of ethanol was added to a suspension of 0.60g (1.7 mmol) of freshly prepared BBDH in 35 cm^3 of the same solvent, and the mixture was stirred for several days to give a pink solid, which was separated by filtration (*Anal:* calcd. for $[Co(BBDH)(H_2O)_2](ClO_4)_2$: C,33.3; H, 3.30; N, 8.64%. Found: C, 33.7;H, 3.53; N, 8.78%). Bubbling CO_2 through the filtrate for 10 h produced deep pink crystals of II.

Anal: calcd. for $[Co_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](ClO_4)_2 \cdot 2H_2O \cdot EtOH$: C, 43.8; H, 3.97; N, 11.11%. Found: C, 44.0; H, 4.09; N, 11.90%. Mass spectrum (*m/z*): 1086 $[Co_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)(ClO_4)]^+$, 985 $[Co_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)]^+$.IR($cm^{-1}$): 3200*s,br* ν(NH), 1622*s* $\nu_{as}(COO^-)$, 1396*m* δ(NH), 1342*s* $\nu_s(COO^-)$, 1094*s,br* $\nu_3(ClO_4^-)$, 684*w* ν(CS), 634*w* $\nu_4(ClO_4^-)$.

Physical measurements

Microanalyses for carbon, hydrogen and nitrogen were performed on a Perkin Elmer 240B microanalyser. Positive ion FAB mass spectra were obtained on a Kratos MS-50 mass spectrometer retrofitted with a Kratos FAB source and interfaced to a Kratos DS-90 data system. IR spectra in the 4000 – 400 cm^{-1} range were recorded in KBr pellets on a Mattson Instruments Cygnus-100 apparatus.

Crystal structure determinations

Crystals suitable for X-ray diffraction studies of **I** and **II** were mounted on glass fibres in a Enraf-Nonius CAD4 diffractometer for data collection. Cell constants were obtained by least-squares refinement of the data for 25 reflections in the range $15° < \theta < 34°$ (**I**) and $6° < \theta < 13°$ (**II**). Data were collected at 293K by the ω/θ scan technique using graphite monochromatized Cu*K*a (λ = 1.54184 Å) radiation for **I** and Mo*K*a (λ = 0.71073 Å) radiation for **II** and were corrected for Lorentz and polarization effects. An empirical absorption correction was also made.[29] A summary of crystal data, experimental details and refinement results is shown in Table I.

TABLE I Crystal data and summary of intensity data collection and structure refinement of $[Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](NO_3)_2\cdot 2H_2O\cdot 2EtOH$(I) and $[CO_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)](ClO_4)_2\cdot 2H_2O\cdot EtOH$ (II)

Compound		*I*	*II*
Colour/shape		Green/prismatic	Pink/prismatic
Size		0.20 × 0.25 × 0.40	0.16 × 0.28 × 0.32
Chemical formula		$C_{48}H_{56}N_{12}Ni_2O_{12}S_4$	$C_{48}H_{56}Cl_2Co_2N_{10}O_{13}S_4$
Formula weight		1238.73	1197.09
Crystal system		Monoclinic	Triclinic
Space group		*C2/c*	*P1*
Unit-cell dim. (Å, °)			
	a	15.371(3)	13.351(5)
	b	13.393(3)	18.960(5)
	c	27.790(4)	11.379(3)
	α	90.00	91.14(2)
	β	99.59(4)	107.93(3)
	γ	90.00	100.88(3)
$V(Å^3)$		5641.0	2681.8
Z		4	2
D_{calc} $(g\ cm^{-3})$		1.458	1.603
μ (mm^{-1})		27.521	10.431
Wavelength radiation		Cu*K* α	Mo*K* α
Refl. measured		4413	9912
Independent refl. $/R_{int}$		3964/0.029	5101/0.036
Observed refl./criterion		$2777/I \geq 3\ \sigma\ (I)$	$2450/I \geq 3\sigma\ (I)$
Maximum value θ (°)		60	20

TABLE I *(Continued)*

Compound	***I***	***II***
Weight	1/σ (*F*)	1/ σ (*F*)
Parameters refined	343	380
R	0.048	0.062
R_w	0.049	0.069
Maximum Δ/σ	0.02	0.01
Δ/ρ $_{\text{max/min}}$ (e Å^{-3})	+0.360/–0.417	+ 1.212/–1,293
Sec. extinction coeff.	6.035×10^{-7}	3.826×10^{-9}

The structures were solved by direct methods and refined on *F* by a full-matrix least-squares procedure. For **I**, anisotropic displacement parameters were used for all non-hydrogen atoms except those of ethanol. For **II**, anisotropic parameters were used for cobalt and the atoms in its coordination sphere and isotropic parameters for other non-hydrogen atoms. Hydrogen atoms were located in a difference Fourier map and added to the structure factor calculations as fixed contributions (B_{iso} = 4.0 Å^2), but their positions were not refined. A secondary extinction correction was applied.[30] Computations were performed by means of VAX-SDP,[31] SHELXS86,[32] SCHAKAL[33] and ORTEPII[34] programs on a DEC MicroVAXII computer. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography*.[35] Fractional atomic coordinates for each compound are given in Tables II and III.

TABLE II Fractional positional parameters for the atoms in [$Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)$]($NO_3$)·$2H_2O$·2EtOH with e.s.d.s in parentheses; for numbering see Figure 1

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}/B_{eq}{}^a$
Metal				
Ni	0.36753(5)	0.22374(7)	0.30267(3)	0.041(4)
1,6-Bis(benzimidazol-2-yl)-2,5-dithiahexane ligands				
S(1)	0.2800(1)	0.3441(19)	0.33998(5)	0.056(8)
S(2)	0.28284(9)	0.0895(1)	0.33083(5)	0.054(89)
N(1)	0.2689(3)	0.2455(3)	0.2425(2)	0.043(2)
N(2)	0.1494(3)	0.3197(3)	0.2024(2)	0.051(3)
N(3)	0.4469(3)	0.2047(3)	0.3691(1)	0.045(2)
N(4)	0.4789(3)	0.1409(4)	0.4441(2)	0.059(3)
C(1)	0.2508(3)	0.2048(4)	0.1955(2)	0.043(3)
C(2)	0.2938(4)	0.1314(4)	0.1729(2)	0.051(3)
C(3)	0.2579(4)	0.1063(5)	0.1250(2)	0.066(4)
C(4)	0.1815(5)	0.1531(5)	0.1015(2)	0.075(4)
C(5)	0.1386(4)	0.2265(5)	0.1229(2)	0.068(4)
C(6)	0.1747(4)	0.2508(4)	0.1705(2)	0.050(3)
C(7)	0.2069(3)	0.3123(4)	0.2442(2)	0.045(3)
C(8)	0.2022(4)	0.3796(5)	0.2866(2)	0.059(4)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}/B_{eq}{}^a$
1,6-Bis(benzimidazol-2-yl)-2,5-dithiahexane ligands				
C(9)	0.2175(4)	0.2593(5)	0.3719(2)	0.075(4)
C(10)	0.1921(4)	0.1616(5)	0.3466(2)	0.069(4)
C(11)	0.3491(4)	0.0667(5)	0.3900(2)	0.058(3)
C(12)	0.4236(4)	0.1395(4)	0.3999(2)	0.050(3)
C(13)	0.5425(4)	0.2126(5)	0.4410(2)	0.055(3)
C(14)	0.6127(4)	0.2446(5)	0.4748(2)	0.069(4)
C(15)	0.6636(4)	0.3200(6)	0.4605(2)	0.074(4)
C(16)	0.6457(4)	0.3594(5)	0.4136(3)	0.071(4)
C(17)	0.5741(4)	0.3281(5)	0.3794(2)	0.059(3)
C(18)	0.5223(3)	0.2528(4)	0.3939(2)	0.048(3)
2-Carboxylatobenzimidazolate dianion				
O(28)	0.4440(2)	0.1218(2)	0.2711(1)	0.042(2)
N(21)	0.4464(3)	0.3267(6)	0.2739(1)	0.038(2)
C(21)	0.4666(3)	0.4239(4)	0.2648(2)	0.039(2)
C(22)	0.4348(4)	0.5138(4)	0.2812(2)	0.051(3)
C(23)	0.4684(4)	0.6011(4)	0.2660(2)	0.058(3)
C(27)	0.5000(–)	0.2737(5)	0.2500(–)	0.035(3)
C(28)	0.5000(–)	0.1647(5)	0.2500(–)	0.037(4)
Nitrate anion				
N(5)	0.0720(4)	0.4292(4)	0.4445(2)	0.072(3)
O(51)	0.0992(3)	0.4420(4)	0.4060(2)	0.102(3)
O(52)	–0.0035(3)	0.4024(4)	0.4449(2)	0.107(4)
O(53)	0.1177(4)	0.4492(5)	0.4836(2)	0.115(4)
Solvents				
O(1)	0.0035(3)	0.5615(3)	0.6850(2)	0.063(2)
O(30)	0.2861(5)	0.3866(6)	0.5280(3)	12.8(2)*
C(30)	0.369(1)	0.360(1)	0.5081(6)	17.9(5)*
C(31)†	0.432(1)	0.379(2)	0.5335(8)	11.2(6)*
C(32)†	0.384(2)	0.415(2)	0.4834(8)	12.4(7)*

$^a U_{eq}$ is defined as one third of the trace of orthogonalized U_{ij}. Starred atoms were refined isotropically; $B_{eq} = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + \ldots]$; †Refined with occupancy factors of 0.5.

TABLE III Fractional positional parameters for the atoms in $[CO_2(BBDH)_2(\mu_2\text{–}O_2C\text{–}BzIm)](ClO_4)\cdot 2H_2O\cdot EtOH$ with e.s.d.s in parentheses; for numbering see Figure 2

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}/B_{eq}{}^a$
Metallic centres				
Co(1)	0.4818(2)	0.8528(1)	0.2508(2)	0.038(1)*
Co(2)	0.2924(2)	0.5791(1)	0.1220(2)	0.032(1)*
1,6-Bis (benzimidazol-2-yl)-2,5-dithiahexane ligands				
S(1)	0.4053(3)	0.9481(2)	0.3352(4)	0.053(2)*
S(2)	0.5888(3)	0.9537(2)	0.1714(4)	0.050(2)*
N(1)	0.3523(9)	0.8615(6)	0.092(1)	0.041(7)*

TABLE III *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}/B_{eq}{}^{a}$
1,6-Bis (benzimidazol-2-yl)-2,5-dithiahexane ligands				
N(2)	0.2130(9)	0.9070(6)	−0.013(1)	3.6(3)
N(3)	0.6123(8)	0.8847(6)	0.4074(9)	0.032(6)*
N(4)	0.7663(9)	0.9509(6)	0.525(1)	3.6(3)
C(1)	0.324(1)	0.8381(8)	−0.035(1)	3.1(3)
C(2)	0.371(1)	0.7957(8)	−0.093(1)	4.0(4)
C(3)	0.320(1)	0.7823(9)	−0.225(2)	5.1(4)
C(4)	0.233(1)	0.8123(9)	−0.283(2)	5.0(4)
C(5)	0.190(1)	0.8523(9)	−0.226(1)	4.3(4)
C(6)	0.237(1)	0.8676(8)	−0.097(1)	3.9(4)
C(7)	0.283(1)	0.9009(8)	0.098(1)	3.7(4)
C(8)	0.282(1)	0.9359(9)	0.213(2)	5.4(4)
C(9)	0.485(1)	1.0272(9)	0.302(1)	4.6(4)
C(10)	0.516(1)	1.0239(9)	0.184(1)	4.6(4)
C(11)	0.705(1)	0.9755(8)	0.302(1)	4.2(4)
C(12)	0.692(1)	0.9359(8)	0.410(1)	3.4(3)
C(13)	0.732(1)	0.9039(7)	0.603(1)	2.9(3)
C(14)	0.776(1)	0.8940(9)	0.726(1)	4.4(4)
C(15)	0.719(1)	0.8425(9)	0.775(1)	4.5(4)
C(16)	0.620(1)	0.8005(9)	0.700(1)	4.7(4)
C(17)	0.578(1)	0.8086(8)	0.575(1)	4.1(4)
C(18)	0.635(1)	0.8627(8)	0.527(1)	3.2(3)
S(21)	0.2733(3)	0.5038(2)	−0.0712(4)	0.045(2)*
S(22)	0.1187(3)	0.4967(2)	0.1212(4)	0.042(2)*
N(21)	0.1935(8)	0.6344(6)	−0.012(1)	0.036(6)*
N(22)	0.1051(9)	0.6517(6)	−0.205(1)	3.4(3)
N(23)	0.3524(8)	0.5061(6)	0.250(1)	0.033(6)*
N(24)	0.3367(9)	0.4170(6)	0.371(1)	3.3(3)
C(21)	0.126(1)	0.6834(8)	−0.011(1)	3.5(3)
C(22)	0.111(1)	0.7152(8)	0.091(1)	3.7(3)
C(23)	0.035(1)	0.7606(9)	0.060(1)	4.5(4)
C(24)	−0.018(1)	0.7714(9)	−0.060(1)	4.5(4)
C(25)	−0.003(1)	0.7390(9)	−0.157(1)	4.9(4)
C(26)	0.073(1)	0.6927(8)	−0.132(1)	3.4(3)
C(27)	0.179(1)	0.6191(8)	−0.130(1)	3.7(4)
C(28)	0.238(1)	0.5713(8)	−0.174(1)	4.0(4)
C(29)	0.144(1)	0.4470(9)	−0.095(1)	4.3(4)
C(30)	0.123(1)	0.4226(8)	0.022(1)	3.7(4)
C(31)	0.173(1)	0.4636(8)	0.269(1)	4.0(4)
C(32)	0.287(1)	0.4635(7)	0.294(1)	2.9(3)
C(33)	0.442(1)	0.4329(8)	0.377(1)	3.3(3)
C(34)	0.529(1)	0.4029(8)	0.444(1)	4.0(4)
C(35)	0.626(1)	0.4338(8)	0.434(1)	4.1(4)
C(36)	0.639(1)	0.4902(8)	0.362(1)	4.1(4)
C(37)	0.551(1)	0.5185(8)	0.293(1)	3.3(3)
C(38)	0.452(1)	0.4883(7)	0.302(1)	2.7(3)
2-Carboxylatobenzimidazolate dianion				
O(31)	0.3800(7)	0.7732(5)	0.3171(8)	0.034(5)*
O(32)	0.3031(7)	0.6573(5)	0.2655(8)	0.038(5)*
N(31)	0.5208(8)	0.7627(6)	0.191(1)	0.033(6)*
N(32)	0.4327(8)	0.6470(6)	0.1257(9)	0.032(6)*
C(41)	0.571(1)	0.7335(8)	0.117(1)	3.5(3)

TABLE III *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/B_{eq}[a]
2-Carboxylatobenzimidazolate dianion				
C(42)	0.661(1)	0.7644(9)	0.081(1)	4.3(4)
C(43)	0.688(1)	0.7210(9)	0.002(1)	4.4(4)
C(44)	0.633(1)	0.6539(9)	−0.044(1)	4.2(4)
C(45)	0.544(1)	0.6210(8)	−0.009(1)	3.8(4)
C(46)	0.513(1)	0.6621(8)	0.074(1)	3.2(3)
C(47)	0.442(1)	0.7068(7)	0.192(1)	2.2(3)
C(48)	0.369(1)	0.7122(7)	0.264(1)	2.2(3)
Perchlorate anions				
Cl(1)	0.9337(4)	0.9476(3)	0.1461(4)	5.8(1)
O(11)	0.951(1)	1.0205(8)	0.184(1)	9.6(4)
O(12)	1.031(1)	0.9345(9)	0.127(1)	9.9(4)
O(13)	0.908(1)	0.905(1)	0.235(2)	11.7(5)
O(14)	0.847(1)	0.935(1)	0.039(2)	12.5(6)
Cl(2)	0.0305(4)	0.6152(3)	0.4400(5)	7.5(1)
O(21)	0.032(2)	0.673(1)	0.362(2)	14.1(6)
O(22)	−0.073(2)	0.591(2)	0.448(3)	23(1)
O(23)	0.027(2)	0.550(2)	0.383(3)	23(1)
O(24)	0.119(2)	0.627(2)	0.540(3)	24(1)
Solvents				
O(40)	1.109(1)	0.9084(7)	0.440(1)	7.9(4)
O(41)	0.207(1)	0.7963(7)	0.401(1)	7.9(4)
O(50)	0.201(1)	0.3299(7)	0.480(1)	7.7(4)
C(50)	0.243(2)	0.282(2)	0.575(3)	12.7(9)
C(51)	0.155(2)	0.221(2)	0.560(3)	13.1(9)

[a] Starred atoms were refined anisotropically. U_{eq} is defined as one third of the trace of orthogonalized U_{ij} and B_{eq} as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + \ldots]$.

RESULTS AND DISCUSSION

In the course of our work on *NSSN* coordination we prepared an ethanolic solution containing equimolar quantities of copper(II) perchlorate and *N*-(2-aminoethyl)-2-{[(piridine-2-yl)methyl]thio}acetamide (synthesized by alkylating *N*-(2-aminoethyl)-2-mercaptoacetamide with 2-picolyl chloride hydrochloride). When left in air and exposed to daylight for several weeks, the expected product was accompanied by crystals of what, when investigated by X-ray diffraction, proved to be copper(II)-*bis*(pyridine-2-carboxylate).[36]

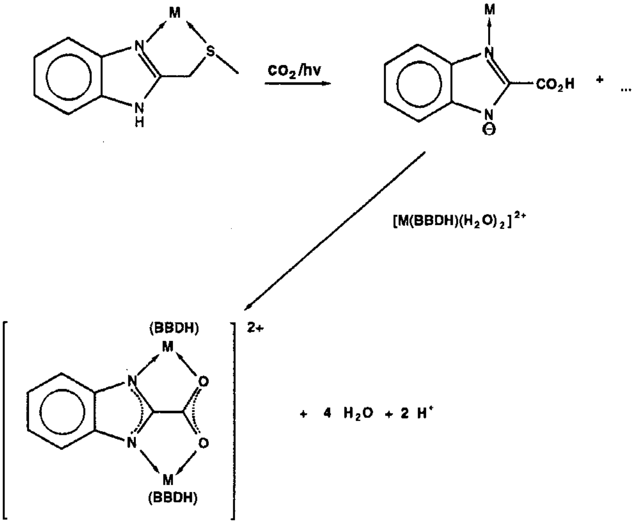
Hypothesizing that similar oxidation reactions might affect other compounds in which a thioether is located on a carbon adjacent to N in a heterocycle, with the S and N atoms both coordinated to a metal, we applied the same conditions to solutions of copper perchlorate and 1,8-*bis*(piridine-2-yl)-3,6-dithiaoctane(bpdto), and nickel(II) nitrate and 1,6-*bis*(benzimidazol-2-yl)-2,5-dithiahexane (BBDH). The former, in keeping with our hypothesis, afforded [(bpdto)copper(II)] diperchlorate, but the latter yielded a mixture of compound **I** and a powder with stoicheiometry $Ni(BBDH)(NO_3)_2 \cdot 2EtOH$.

Since compound **I** was interpreted as being the result of the oxidation of BBDH, experiments were carried out in which oxidizing agents (including hydrogen peroxide) were included in the reaction mixture with $Ni(NO_3)_2$ and BBDH, but under these condictions no **I** was produced.[37] In view of this, the TMC-catalysed fixation of CO_2 by BBDH was suspected, and a strong current of CO_2 was bubbled through an ethanolic solution of $Ni(NO_3)_2$ and BBDH. As hoped, the powdery product appeared, from its IR spectrum, to contain a carboxylate group. Similar results were obtained when 1,7-*bis*(benzimidazol-2-yl)-2,6-dithiaheptane (BBDHP) was used instead of BBDH. The photochemical nature of the reaction was confirmed by the absence of ν(CO) bands in the IR spectrum of the product obtained when CO_2 was bubbled in the absence of visible light. Finally, in fulfilment of our predictions, the reaction with $Co(ClO_4)_2$ and BBDH afforded crystals of compound **II**.

Mechanism

A plausible mechanism for the above reactions is shown in Scheme I. The $[O_2C\text{-}BzIm]^{2-}$ ion contained in **I** and **II** (see below) can only come from the cleavage of a benzimidazole-thioether bond. Cleavage of this bond *via* attack by CO_2 is no doubt facilitated by the coordination of the metal to both the neighbouring sulphur atom (which coordination must weaken the benzimidazole-thioether bond) and to the non-protonated benzimidazole nitrogen atom (which is thereby protected from attack, as in the syntheses[27] of 1H-imidazole-2-carboxylic acids mentioned in the Introduction). Then, cleavage of the benzimidazole-thioether bond having been followed by bonding between the CO_2 and the benzimidazole moiety; the M—S bond is probably replaced by M—O coordination, the thioether chain thereby being released into solution. The possibility that in solution the sulphur atom is not coordinated to the metal in the first place would appear to be argued against by the fact that in subsequent work[36] we have been able to generalize this reaction only to thioethers bearing terminal heterocycles allowing the formation of C—S—M—N—C chelate ring. Finally, the coordination of the 2 carboxylatobenzimidazolato ion to its original metal must be replaced by coordination to the metal atoms of two intact $[M(BBDH)(H_2O)_2]^{2+}$ ions.

Note that the above mechanism differs from that proposed[38] for the synthesis of copper(I) pyrazolecarboxylate complexes by the action of CO_2 on suspensions of copper pyrazolates at high temperature. For the latter synthesis, initial formation of the free pyrazolecarboxylic acid (by reaction between CO_2 and excess pyrazole)



Scheme 1

is thought to be essential, whereas the mechanism of Scheme I involves the formation of no free acid.

Description of the structure of I

The molecular structure of $[Ni_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)]^{2+}$ is shown in Figure 1 together with the atom numbering scheme used; main bond lengths and angles are listed in Table IV. Crystals of **I** consist of discrete $[Ni(BBDH)(\mu_2\text{-}O_2C\text{-}BzIm)(BBDH)Ni]^{2+}$ cations separated by nitrate anions, molecules of water and ethanol of crystallization (two molecules per cation). The cations have crystallographically imposed C_2 symmetry about an axis that contains the C(28)-C(27) bond and bisects both C(21)-C(21^i) and C(23)-C(23^i). The distance between the two Ni atoms, 5.397(2) Å, rules out orbital interactions between them.

The coordination polyhedron of the Ni atoms is a slightly distorted octahedron. As in other BBDH complexes,[39-47] the axial positions are occupied by benzimidazole nitrogen atoms and two *cis* equatorial positions by the thioether sulphur atoms. The remaining equatorial positions are occupied by one N and one O atom of the bridging 2-carboxylatobenzimidazolato ion. The nickel atoms lie just 0.004 Å from the planes defined by their equatorial atoms, and these planes are coplanar with the planar $[O_2C\text{-}BzIm]^{2-}$ ion. Distortion of the coordination polyhedron shows up in the angles of the equatorial plane, with *cis* angles ranging from 82.4(1)° for O(28)—Ni—N(21) to 98.6(1)° for S(1)—Ni—N(21) and *trans* angles of 172.1(1)° for S(2)—Ni—N(21) and 178.8(2)° for

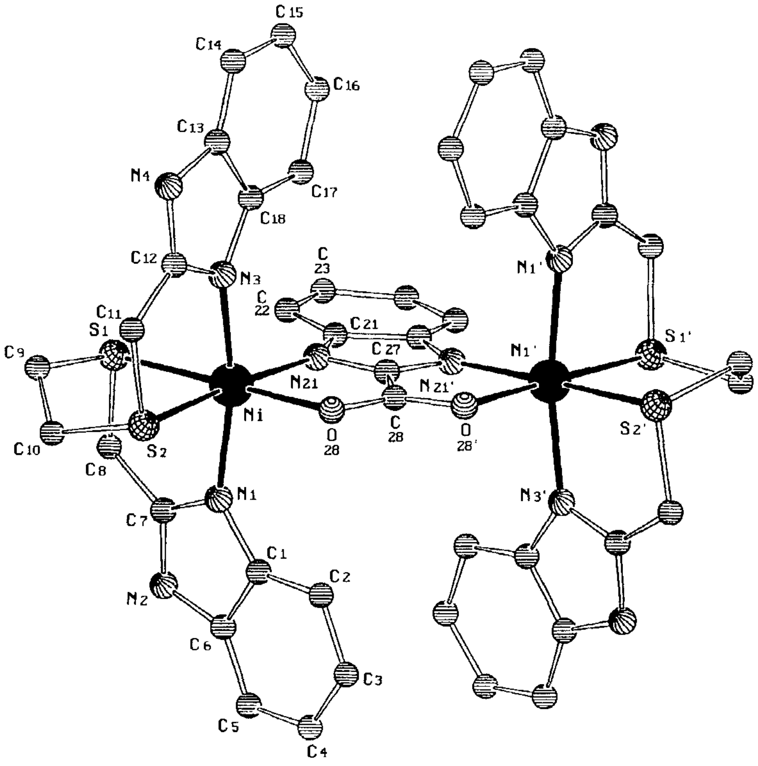


FIGURE 1 Perspective view of the molecular structure of $[Ni(BBDH)(\mu_2\text{-}O_2C\text{-}BzIm)(BBDH)Ni]^{2+}$ showing the atom numbering scheme for non-hydrogen atoms. H atoms are omitted for clarity. Symmetry code: i = 1–x, y, 0.5–z.

S(1)—Ni—O(28), and in the axial N(1)—Ni—N(3) angle of 169.8(2)°. The latter lies in the range 163.2(1)–173.9(2)° of reported axial angles in hexacoordinate complexes of Ni(II) with BBDH.[37,43–46]

TABLE IV Compound I: main bond distances (Å) and angles (°)

Coordination Sphere			
Distances			
Ni—S(1)	2.413(2)	Ni—S(2)	2.455(2)
Ni—N(1)	2.078(4)	Ni—N(3)	2.059(4)
Ni—O(28)	2.114(3)	Ni—N(21)	2.055(4)
Angles			
S(1)—Ni—S(2)			89.29(6)
S(1)—Ni—N(1)	83.3(1)	S(2)—Ni—N(1)	89.6(1)
S(1)—Ni—N(3)	89.9(1)	S(2)—Ni—N(3)	82.7(1)

TABLE IV *(Continued)*

COORDINATION SPHERE			
Angles			
S(1)—Ni—O(28)	178.8(2)	S(2)—Ni—O(28)	89.7(2)
S(1)—Ni—N(21)	98.6(1)	S(2)—Ni—N(21)	172.1(1)
O(28)—Ni—N(1)	97.3(1)	O(28)—Ni—N(3)	89.4(1)
O(28)—Ni—N(21)	82.4(1)	N(1)—Ni—N(3)	169.8(2)
N(1)—Ni—N(21)	90.3(2)	N(3)—Ni—N(21)	98.3(2)
2-CARBOXYLATOBENZIMIDAZOLATE DIANION			
Distances			
O(28)—C(28)	1.259(5)	C(27)—C(28)	1.460(10)
N(21)—C(21)	1.371(6)	N(21)—C(27)	1.343(6)
C(21)—C(21^{i})	1.419(7)	C(23)—C(23^{i})	1.421(9)
C(21)—C(22)	1.404(8)	C(22)—C(23)	1.372(9)
Angles			
N(21)—C(21)—C(21^{i})	108.3(4)	N(21)—C(21)—C(22)	130.9(5)
C(21^{i})—C(21)—C(22)	120.8(5)	C(21)—C(22)—C(23)	117.5(5)
C(22)—C(23)—C(23^{i})	121.6(5)	N(21)—C(27)—C(28)	121.9(3)
O(28)—C(28)—O(28^{i})	125.6(6)	N(21)—C(27)—N(21^{i})	116.2(6)
O(28)—C(28)—C(27)			117.2(3)

Symmetry code i = *1–x, y, 0.5–z.*

The Ni—S bond lengths, 2.413(2) and 2.455(2) Å, are slightly greater than the sum of the covalent radii (2.36 Å),[48] but well within the range 2.379(1)–2.516(1) Å of reported equatorial Ni—S distances,[37, 43–46, 49–54] although the value 2.455(2) Å is rather greater than the mean for Ni—S bonds in hexacoordinate nickel complexes, 2.416 Å.[55] The three Ni—N distances, 2.078(4), 2.059(4) and 2.055(4) Å, are all rather shorter than the sum of the covalent radii (2.09 Å);[48] they are similar to Ni—N distances found in many octahedral complexes of nickel(II) with *NSSN* ligands in which the donor nitrogen atoms belong to benzimidazolyl groups,[37, 43–46, 49] but are shorter than those observed when the terminal heterocycles are pyridine rings, which range from 2.104 to 2.142 Å.[52–54] The Ni—O distance, 2.114(3) Å is longer than the sum of the covalent radii (2.05 Å)[48] and also longer than those found in $[Ni_2(bpdto)_2(\mu_2\text{-}C_2O_4)]^{2+}$ [2.056(2) and 2.058(2) Å],[54] but is more similar to the values 2.137(4) and 2.109(4) Å found in $[Ni(BBDH)(\eta^2\text{-}O_2CCH_3)]^{+}$[44]

Each BBDH molecule is not only coordinated to a nickel atom but is also hydrogen-bonded[55] *via* its *H*-bearing non-donor benzimidazole N atoms to two O atoms of the neighbouring nitrate ion and to the O atom of the neighbouring water molecule, which is also hydrogen-bonded *via* its own hydrogen atoms to the third nitrate O atom and to the nearest carboxylate O atom (Table V). The bond angles at the thioether sulphur atoms, 103.5(3)° for C(8)—S(1)—C(9) and 102.2(3)° for C(10)—S(2)—C(11), confirm that one of the sulphur lone pairs is

TABLE V Hydrogen bond data for compounds **I** and **II**

A-H···B	*A-H(Å)*	*H···B(Å)*	*A···B(Å)*	*A-H-B(°)*
COMPOUND ***I***				
O(1^{i})—H(10)—O(28^{ii})	0.950(4)	1.850(3)	2.800(5)	175.5(2)
O(1^{i})—H(11)—O(51)	(4)	1.947(4)	2.750(7)	166.6(3)
N(2)—H(20)—O(1^{iii})	1.045(4)	1.743(4)	2.726(6)	155.1(3)
N(4)—H(40)—O(52^{iv})	1.016(5)	2.154(6)	3.099(8)	153.8(3)
N(4)—H(40)—O(53^{iv})	1.016(5)	2.143(6)	2.948(8)	134.7(3)
Symmetry codes: i = *–x, 1–y, 1–z;* ii = *x–0.5, 0.5+y, z;* iii = *2–x, 2–y, 1–z;* iv = *–x, 1–y, 1–z*				
COMPOUND ***II***				
N(2)—H(02)—O(11^{i})	0.977(13)	2.195(15)	3.012(19)	140.2(9)
N(4)—H(04)—O(40^{ii})	0.974(11)	1.961(13)	2.816(17)	145.2(9)
N(22)—H(022)—O(24^{iii})	0.971(11)	2.144(37)	2.996(38)	145.7(11)
N(24)—H(024)—O(50)	0.971(12)	1.883(15)	2.810(19)	158.6(9)
O(50) · · · O(22^{iv})			2.765(40)	
O(40) · · · O(13)			2.949(20)	
O(41) · · · O(21)			2.892(23)	
Symmetry codes: i = *1–x, 2–y, –z;* ii = *2–x, 2–y, 1–z;* iii = *x, y, z–1;* iv = *–x, 1–y, 1–z*				

pulled strongly towards the nickel atom. The benzimidazole moieties are essentially planar (none of the benzimidazole atoms is further than 0.025 Å from the corresponding least-squares plane), and their planes meet with a dihedral angle of 87.4(1)°.

Description of the structure of II

The asymmetric unit of crystals of **II** comprises a $[Co_2(BBDH)_2(\mu_2\text{-}O_2C\text{-}BzIm)]^{2+}$ cation, two perchlorate anions, two water molecules and a molecule of ethanol. The anions, water and ethanol exhibit considerable disorder. The molecular structure of the cation, consisting of two Co(BBDH) units linked by a bridging 2-carboxylatobenzimidazolato unit, is shown in Figure 2 together with the atom numbering scheme used; the Co—Co distance is 5.285(6) Å, and other main bond lengths and angles are listed in Table VI. Each metal atom has a distorted octahedral coordination polyhedron, the positions of which are occupied by the same BBDH and 2-carboxylatobenximidazolato atoms as in **I**. However, distortion of the coordination polyhedron is greater than in **I**, with *cis* equatorial angles ranging from 79.7(4)° to 103.5(4)° for Co(1) and from 79.2(3)° to 100.8(5)° for Co(2), *trans* equatorial angles of 168.9(3)–178.8(4)°, and axial N—Co—N angles of 158.8(5)° for Co(1) and 165.2(4)° for Co(2). Note that the N—Co—N angles are both outside the range hitherto observed in octahedral complexes of cobalt(II) with BBDH[39–42] 160.9–165.1°. Co(1) and Co(2) lie, respectively, 0.043 and 0.092Å from the least-squares planes through their equatorial atoms, which

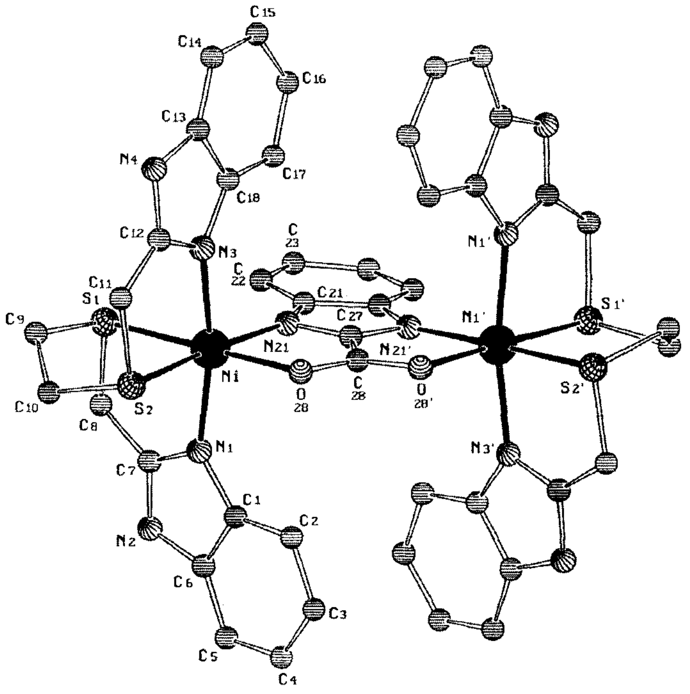


FIGURE 2 Perspective view of the [Co(BBDH)(μ_2-O_2C-BzIm)(BBDH)Co]$^{2+}$ cation showing the atom numbering scheme and the coordination geometry about each cobalt atom. H atoms are omitted for clarity.

meet at a dihedral angle of 39.9(2)°. The planar [O_2C-BzIm]$^{2-}$ anion forms dihedral angles of 23.5° with the equatorial plane of Co(1) and 16.9° with that of Co(2).

TABLE VI Compound II: main bond distances (Å) and angles (°)

Coordination Sphere			
Distances			
Co(1)—S(1)	2.542(6)	Co(2)—S(21)	2.515(5)
Co(1)—S(2)	2.519(5)	Co(2)—S(22)	2.536(4)
Co(1)—N(1)	2.114(10)	Co(2)—N(21)	2.124(11)
Co(1)—N(3)	2.055(9)	Co(2)—N(23)	2.113(11)
Co(1)—O(31)	2.144(10)	Co(2)—O(32)	2.136(10)
Co(1)—(31)	2.038(12)	Co(2)—N(32)	2.052(10)
Angles			
S(1)—Co(1)—S(2)	87.3(2)	S(21)—Co(2)—S(22)	85.5(1)
S(1)—Co(1)—N(1)	79.7(4)	S(21)—Co(2)—N(21)	80.7(3)
S(1)—Co(1)—N(3)	84.3(4)	S(21)—Co(2)—N(23)	97.0(3)
S(1)—Co(1)—O(31)	87.9(3)	S(21)—Co(2)—O(32)	170.2(3)

TABLE VI (*Continued*)

Coordination Sphere			
Angles			
S(1)—Co(1)—N(31)	168.9(3)	S(21)—Co(2)—N(32)	95.7(3)
S(2)—Co(1)—N(1)	85.3(3)	S(22)—Co(2)—N(21)	86.1(3)
S(2)—Co(1)—N(3)	80.1(3)	S(22)—Co(2)—N(23)	79.2(3)
S(2)—Co(1)—O(31)	174.7(3)	S(22)—Co(2)—O(32)	98.0(3)
S(2)—Co(1)—N(31)	103.5(4)	S(22)—Co(2)—N(32)	178.8(4)
N(1)—Co(1)—N(3)	158.8(5)	N(21)—Co(2)—N(23)	165.2(4)
N(1)—Co(1)—O(31)	91.5(4)	N(21)—Co(2)—O(32)	90.4(4)
N(1)—Co(1)—N(31)	98.9(4)	N(21)—Co(2)—N(32)	94.0(4)
N(3)—Co(1)—O(31)	101.8(4)	N(23)—Co(2)—O(32)	92.6(4)
N(3)—Co(1)—N(31)	99.4(4)	N(23)—Co(2)—N(32)	100.8(5)
O(31)—Co(1)—N(31)	81.1(4)	O(32)—Co(2)—N(32)	80.8(4)
2-Carboxylatobenzimidazolate Dianion			
Distances			
O(31)—C(48)	1.255(16)	O(32)—C(48)	1.232(15)
C(47)—C(48)			1.472(22)
N(31)—C(47)	1.347(16)	N(32)—C(47)	1.314(17)
N(31)—C(41)	1.394(21)	N(32)—C(46)	1.372(20)
C(41)—C(42)	1.417(24)	C(45)—C(46)	1.410(24)
C(42)—C(43)	1.379(26)	C(44)—C(45)	1.403(24)
C(43)—C(44)	1.349(20)	C(41)—C(46)	1.419(19)
Angles			
C(41)—N(31)—C(47)	102.1(11)	C(46)—N(32)—C(47)	104.3(11)
N(31)—C(41)—C(42)	130.6(13)	N(31)—C(41)—C(46)	108.2(13)
C(42)—C(41)—C(46)	121.2(15)	C(41)—C(42)—C(43)	115.9(14)
C(42)—C(43)—C(44)	124.1(17)	C(43)—C(44)—C(45)	121.8(17)
C(44)—C(45)—C(46)	116.8(13)	C(41)—C(46)—C(45)	120.2(14)
N(32)—C(46)—C(45)	132.0(12)	N(32)—C(46)—C(41)	107.8(14)
N(31)—C(47)—N(32)	117.5(13)	O(31)—C(48)—O(32)	127.0(14)
N(31)—C(47)—C(48)	121.0(11)	N(32)—C(47)—C(48)	121.0(11)
O(31)—C(48)—C(47)	115.6(11)	O(32)—C(48)—C(47)	117.3(12)

The Co—S distances, which range from 2.515(5) to 2.542(6) Å, are within the range reported for octahedral Co(II) complexes with *NSSN* ligands.[39–42, 56] Co—N distances, 2.038(12)–2.124(11) Å, are in keeping with the mean value of 2.116 Å found for other octahedral complexes of Co(II) with BBDH, and with the value of 2.103 Å reported for Co—N(imidazole).[54] The Co—O distances, 2.144(10) and 2.136(10) Å, are significantly longer than the mean value observed in octahedral cobalt(II) complexes with $[\mu_2\text{-}O_2CC(sp^2)]$ units.[54]

Bond lengths and bond angles of the BBDH ligands are all within expected ranges. The benzimidazolyl moieties are planar, with maximum deviations of only 0.0001–0.0293 Å from the corresponding least-squares planes, and the dihedral angles between the benzimidazolyl moieties within the BBDH ligands are 95.8(3)° for one ligand and 69.2(3)° for the other.

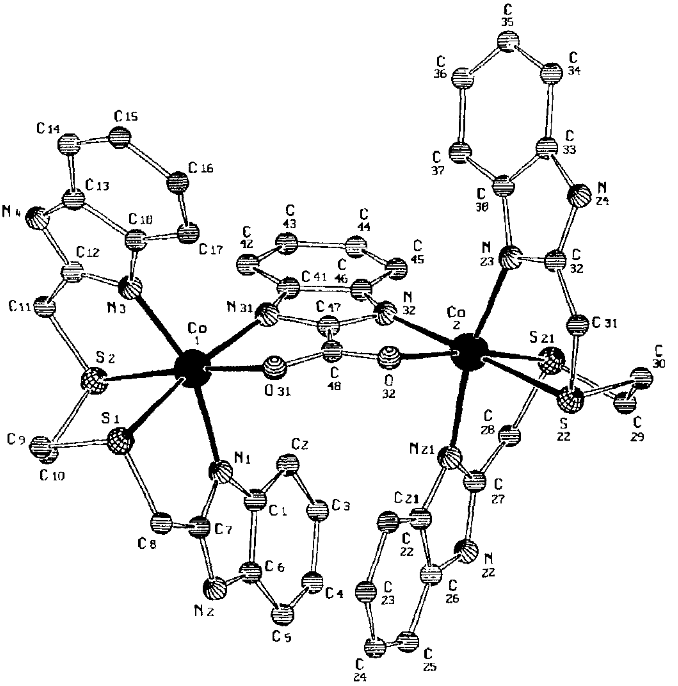


FIGURE 3 ORTEP representation of the dianion 2-carboxylatobenzimidazolate, $[O_2C\text{-BzIm}]^{2-}$, as extracted from the data for compound **II**. Thermal ellipsoids represent 50% probability surfaces.

The crystal structure of II is stabilized by hydrogen bonds[55] between benzimidazolyl NH groups and oxygen atoms belonging to the perchlorate anions and water and ethanol molecules (Table V). Some of the O—O distances between perchlorate anions and molecules of crystallization (namely, the three between 2.765 and 2.949 Å) are also suggestive of hydrogen bonds.

Description of the structure of $[O_2C\text{-BzIm}]^{2-}$

As noted above, the 2-carboxylatobenzimidazolato dianion (Figure 3) is planar in both **I** and **II**; no $[O_2C\text{—BzIm}]^{2-}$ atom lies further than 0.025 Å from the least-squares plane. Furthermore, the maximum distance between this plane and a metal atom is 0.057(1) Å. The C—O bond lengths, 1.232(15)–1.259(5) Å, do not differ significantly from those observed in dinuclear complexes with oxalato[57] or carboxylato $([\mu_2\text{-}O_2CC(sp^2)])$[54] bridges, or from the value of 1.282 Å found in the CO_2^- radical anion.[7] The O—C—O angles, 125.6(6)° in **I** and 127.0(14)° in **II**, are within the range reported for the oxalato dianion,[58] but are rather smaller than those (127–138°) exhibited by diverse species containing the CO_2^- radical anion.[7] The length of the C—C bond between the carboxylato and benzimidazolato moieties, 1.460(10) Å in **I** and 1.472(22) Å in **II**, being somewhat less than that (1.545 Å) of typical single bonds, is indicative of slight double bond character (rather more than in [μ_2–$O_2CC(sp^2)$] complexes, for which the mean length of this bond is 1.493 Å.[54] The C—N and C—C distances in the benzimidazolato moiety do not differ significantly from those of the benzimidazolyl groups of **I**, **II** or other BBDH complexes.[39–45]

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SUPPLEMENTARY DATA

Full list of hydrogen coordinates, bond lengths and angles, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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