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Synthesis, X-ray and spectroscopic characterisation of chromium(III) coordination compounds with benzimidazolic ligands

Agueda E. Ceniceros-Gómez [a], Noráh Barba-Behrens [a], M. Elba Quiroz-Castro [a],
Sylvain Bernès [b], Heinrich Nöth [c], Silvia E. Castillo-Blum [a,*]

[a] *Departimento de Química Inorgánica, Facultad de Química, UNAM, Ciudad Universitaria, 04510 Mexico D.F., Mexico*
[b] *USAI, Facultad de Química, UNAM, Ciudad Universitaria, 04510 Mexico D.F, Mexico*
[c] *Institute of Inorganic Chemistry, University of Munich, Bütenandtstraße 5-13, Haus D, D-81377 Munich, Germany*

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Abstract

The syntheses and characterisation of chromium(III) complexes with tris(2-benzimidazolylmethyl)amine (ntb), 2-guanidinobenzimidazole (2gb), 2,6-bis(2-benzimidazolyl)pyridine (bbimpy) and 2-(2-pyridyl)benzimidazole (2pb), of composition $[Cr(ntb)Cl_2]Cl{\cdot}4.5H_2O$ (**1**), $[Cr(2gb)_3]Cl[ZnCl_4]{\cdot}CH_3OH$ (**2**), $[Cr(2gb)_3]Cl_3{\cdot}4H_2O$ (**3**), $[Cr_2(2gb)_4(\mu\text{-}OH)_2](ClO_4)_4{\cdot}5H_2O$ (**4**), $[Cr(bbimpy)Cl_3]$ (**5**) and $[Cr(2pb)_2Cl_2]Cl{\cdot}C_2H_5OH{\cdot}0.5H_2O$ (**6**) are presented. The compounds are obtained from Cr(III) in alcoholic solution, or a Cr(II) aqueous acidic solution. The latter were carried out under air-free conditions. The reaction of 2gb with Cr(II) in aqueous solution yielded a dinuclear compound. The X-ray crystal structures of **1** and **4** are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Chromium(III) complexes; Tris(2-benzimidazolylmethyl)amine; 2-Guanidinobenzimidazole; 2,6-Bis(2-benzimidazolyl)pyridine; 2-(2-Pyridyl)benzimidazole; Crystal structures

1. Introduction

Imidazole is a typical heterocyclic ligand with nitrogen as the donor atom. It is also a component of biologically important molecules [1]. Because of this, the coordination chemistry of related ligands has been the subject of numerous investigations [1]. Amongst them, the coordinating behaviour of chelating benzimidazolic ligands has been studied by several research groups, some of them with an interest in mimicking biological activities [2–6]. Benzimidazoles exhibit a wide variety of pharmacological activities like fungicides or anti-helminthics amongst others [7]. Studies about the coordination chemistry of benzimidazolic ligands have been carried out mainly on labile metal ions [1,8–10]. It is worth mentioning that there are only a limited number of reports on chromium(III) complexes containing imidazoles [11–14] or benzimidazoles [14,15]. The synthesis, reactivity and magnetic properties of dinuclear chromium(III) species containing OH^- bridges have been studied for the last two decades [16,17]. However, none of them contained imidazolic or benzimidazolic ligands.

We have been interested in the coordinating ability of benzimidazolic ligands towards transition metal ions [8,18,19]. Here we describe the synthesis and characterisation of substitution inert chromium(III) coordination compounds with four benzimidazolic ligands. The X-ray crystal structures of $[Cr(ntb)Cl_2]Cl{\cdot}2H_2O{\cdot}C_2H_5OH$ and $[Cr_2(2gb)_4(\mu\text{-}OH)_2](ClO_4)_4{\cdot}4.67H_2O$ are discussed.

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* Corresponding author. Tel.: + 52-5-622-3812; fax: + 52-5-622-3724.

E-mail address: blum@servidor.unam.mx (S.E. Castillo-Blum).

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2. Experimental

2.1. Materials

Metallic chromium, zinc and mercury, anhydrous $CrCl_3$, $CrCl_2$, $CrCl_3 \cdot nH_2O$, 2-guanidinobenzimidazole (2gb), 2,6-bis(2-benzimidazolyl)pyridine (bbimpy), 2-(2-pyridyl)benzimidazole (2pb) and tris(2-benzimidazolylmethyl)amine (ntb), methanol, ethanol and $HClO_4$ were used as analytical reagents and obtained from Aldrich. They were used without further purification.

2.2. Syntheses

2.2.1. $[Cr(ntb)Cl_2]Cl \cdot 4.5H_2O$ (**1**)

Anhydrous $CrCl_3$ (0.158 g, 1.00 mmol) was placed in the filter thimble of a Soxhlet extractor together with Zn–Hg amalgam (1 cm^3), and a solution of ntb (0.407 g, 1.00 mmol) in anhydrous methanol (50 cm^3) was added to the reservoir flask. N_2 was bubbled through the ntb solution for 10 min before heating and chromium chloride was then extracted as a green solution that reacted with ntb. A green precipitate formed and was isolated by vacuum filtration (0.270 g, 42.3%). (Found: C, 44.65; H, 4.20; N, 14.90. $C_{24}H_{20}N_7CrCl_3 \cdot 4.5H_2O$ requires C, 44.56; H, 4.67; N, 15.16%). Green crystals of **1** (minimum formula $C_{26}H_{31}O_3N_7CrCl_3$) were obtained simply by mixing the solutions of $CrCl_3 \cdot nH_2O$ and ntb in ethanol and leaving the solution to stand for few days.

2.2.2. $[Cr(2gb)_3]Cl[ZnCl_4] \cdot CH_3OH$ (**2**), $[Cr(2gb)_3]Cl_3 \cdot 4H_2O$ (**3**)

Anhydrous $CrCl_3$ (1.0 g, 6.3 mmol) and Zn powder (10 mg) were stirred together in anhydrous methanol (50 cm^3). A solution of 2gb (3.31 g, 18.9 mmol) in hot anhydrous methanol was added with stirring. The mixture was heated (40°C) with stirring for 3 h. A pink solid precipitated immediately **2**, which was filtered off. The red solution deposited small red crystals of **3** by slow evaporation. Compound **2**: (0.128 g, 2.4%). (Found: C, 35.20; H, 4.47; N, 25.38. $C_{25}H_{31}ON_{15}$-$CrZnCl_5$ requires C, 35.23; H, 3.68; N, 24.65%). Compound **3**: (4.50 g, 95.2%). (Found: C, 38.13; H, 4.15; N, 27.16. $C_{24}H_{35}O_4N_{15}CrCl_3$ requires C, 38.13; H, 4.67; N, 27.79%).

2.2.3. $[Cr_2(2gb)_4(\mu\text{-}OH)_2](ClO_4)_4 \cdot 5H_2O$ (**4**)

A solution of 2gb (0.525 g, 3.00 mmol) in methanol (30 cm^3) was deoxygenated with N_2 in a vacuum line. Chromium metal (0.32 g, 6.00 mmol), or $CrCl_2$ (0.737 g, 6.00 mmol), was dissolved in 6 cm^3 of deoxygenated 2.0 M $HClO_4$. 1.0 cm^3 of this chromium(II) solution was injected into the 2gb solution. Air was allowed into the flask, and 2.0 g of $NaClO_4$ was added. X-ray quality purple crystals deposited from the solution, which were filtered off (0.635 g, 48.1%). (Found: C, 28.74; H, 3.41; N, 20.85. $C_{32}H_{48}O_{23}N_{20}Cr_2Cl_4$ requires C, 28.97; H, 3.65; N, 21.12%).

2.2.4. $[Cr(bbimpy)Cl_3]$ (**5**)

Anhydrous $CrCl_3$ (0.158 g, 1.00 mmol) was placed in the filter thimble of a Soxhlet extractor together with Zn–Hg amalgam (1 cm^3). A solution of bbimpy (0.622 g, 2.00 mmol) in anhydrous ethanol (60 cm^3) was placed into the reservoir flask. N_2 was bubbled through the ligand solution for 10 min before heating and chromium chloride was then extracted as a green solution that reacted with the bbimpy ligand. A green solid precipitated and was isolated by vacuum filtration (0.435 g, 92.6%). (Found: C, 48.77; H, 2.95; N, 14.82. $C_{19}H_{13}N_5CrCl_3$ requires C, 48.59; H, 2.80; N, 14.90%).

2.2.5. $[Cr(2pb)_2Cl_2]Cl \cdot C_2H_5OH \cdot 0.5H_2O$ (**6**)

Anhydrous $CrCl_3$ (0.158 g, 1.0 mmol) was placed in the filter thimble of a Soxhlet extractor together with Zn–Hg amalgam (1 cm^3) and a solution of 2pb (0.585 g, 3.0 mmol) in anhydrous ethanol (60 cm^3) was added to the reservoir flask. N_2 was bubbled through the ligand solution for 10 min before heating and the chromium chloride was then extracted as a green solution that reacted with the 2pb ligand. A green precipitate formed and was isolated by vacuum filtration (0.294 g, 49.5%). (Found: C, 51.65; H, 4.02; N, 13.99. $C_{24}H_{18}N_6CrCl_3 \cdot C_2H_5OH \cdot 0.5H_2O$ requires C, 51.71; H, 4.17; N, 13.92%).

2.3. Physical measurements

An FT-IR spectrometer (Perkin–Elmer 1600) was used for obtaining IR spectra of solid samples in KBr pellets (4000–400 cm^{-1}). The UV–Vis spectra (diffuse reflectance) were recorded on a Cary-5E (Varian) spectrometer (250–2500 nm). Elemental analyses were carried out with a Fisons EA 1180 analyser. Magnetic susceptibility measurements of powdered samples were recorded on a Johnson–Matthey DG8 5HJ balance using the Gouy method. Magnetic susceptibilities were measured on powdered samples of **4** in the temperature range 17–280 K using a Vibrating Sample Magnetometer Model 4500 from EG & G PARC.

2.4. Crystallography

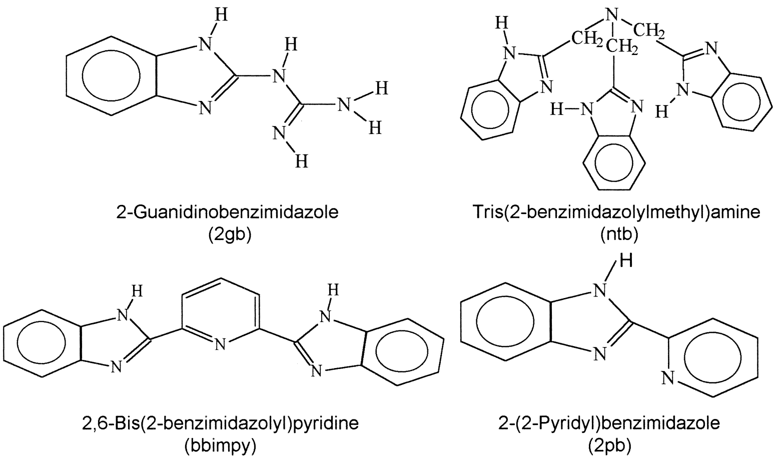
Pertinent crystal data for **1** and **4** are given in Table 1. The diffraction data for **4** were collected at 298 K on a Siemens P4 diffractometer in the 2θ range 3–50° ($\lambda = 0.71073$ Å) at variable scan speed in ω (4–60° min^{-1}). Data were corrected for absorption using 12 ψ-scans with χ close to 90° (min = 0.712, max = 0.758). Data for **1** were collected at 183 K with the crystal mounted on a glass fibre coated with perfluorpolyether

Table 1
Crystallographic data for compounds **1** and **4**

	1	**4**
Formula	$[Cr(C_{24}H_{21}N_7)Cl_2]Cl$ $(C_2H_5OH)(H_2O)_2$	$[Cr_2(C_8H_9N_5)_4(OH)_2]$ $(ClO_4)_4(H_2O)_{4.67}$
M	647.93	1320.70
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.3057(2)	12.156(2)
b (Å)	13.4632(3)	14.035(2)
c (Å)	21.5037(3)	16.733(3)
α (°)		90.04(1)
β (°)	103.103(1)	110.18(1)
γ (°)		106.96(1)
U (Å^3)	2905.91(9)	2546.7(6)
Z	4	2
D_{calc} (Mg m^{-3})	1.481	1.722
F(000)	1340	1353
μ(Mo Kα) (mm^{-1})	0.711	0.738
Crystal dimensions (mm)	$0.32\times0.25\times0.18$	$0.6\times0.4\times0.4$
Total reflections measured	16 066	10 303
Number of unique reflections	5802	8917
Number of observed reflections [$F_o>4\sigma(F_o)$]	3791	6646
Number of variables	362	739
Goodness of fit [a]	1.501	1.034
R_1 (observed data) [a]	6.62	5.91
wR_2 (all data) [a]	12.64 [b]	18.24 [c]

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2=\sqrt{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2}$, $S=\sqrt{\Sigma w(F_o^2-F_c^2)^2/m-n}$.
[b] $w=[\sigma^2(F_o^2)+(0.0210P)^2+7.6749P]^{-1}$.
[c] $w=[\sigma^2(F_o^2)+(0.0959P)^2+4.42P]^{-1}$.

oil. 1200 frames were measured on a Siemens P4 diffractometer equipped with an area detector in the hemisphere scan mode ($\phi=0$–360°, 10 s exposure per frame), which corresponds to the 2θ range 3–58° ($\lambda=0.71073$ Å). Absorption correction was applied using SADABS [20] (min = 0.804, max = 0.883). Both structures were solved and refined using SHELXTL 5.03 [21] and SHELX-97-2 [22], without constraints or restraints for non-H atoms. Most of the H atoms were placed on idealised positions and refined using a riding model with a fixed isotropic U factor. H atoms for the OH groups in **4** and for the water molecules in **1** were found on difference maps and refined as remaining H. In the case of **4**, H atoms were omitted for the water molecules.



2-Guanidinobenzimidazole (2gb)

Tris(2-benzimidazolylmethyl)amine (ntb)

2,6-Bis(2-benzimidazolyl)pyridine (bbimpy)

2-(2-Pyridyl)benzimidazole (2pb)

Fig. 1. Structures of the benzimidazolic ligands.

Table 2
Spectroscopic UV–Vis, IR and magnetic data for **1**–**6**

Compound	Uv–Vis			IR				μ_{eff}
	ν_1 (cm^{-1})	ν_2	ν_3	ν(N–H) (cm^{-1})	ν(C=C) + ν(C=N)	δ(N–H)	δ(C–H)	M.B.
ntb				3384	1622, 1536	1438	742	
1 $[Cr(ntb)Cl_2]Cl\cdot4.5H_2O$	16 650	23 050	28 580	3384	1622, 1594	1450	744	3.9
2gb				3140	1648 [a], 1598 [a], 1540	1450	740	
2 $[Cr(2gb)_3]Cl(ZnCl_4)\cdot CH_3OH$	20 050	25 050	28 650	3190	1666 [a], 1634 [a], 1556	1486	744	3.9
3 $[Cr(2gb)_3]Cl_3\cdot4H_2O$	19 723	25 320	28 010	3190	1668 [a], 1634 [a], 1556	1486	744	3.9
4 $[Cr_2(2gb)_4(\mu\text{-}OH)_2](ClO_4)_4\cdot5H_2O$	17 360	24 570	36 100	3194	1667 [a], 1560	1466	749	4.96 [b]
bbimpy				3055	1599, 1588, 1571	1459	741	
5 $[Cr(bbimpy)Cl_3]$	16 660	20 000	25 000	3068	1607, 1590, 1575	1467	753	3.8
2pb				3056	1593, 1567,	1442, 1400	743	
6 $[Cr(2pb)_2Cl_2]Cl\cdot0.5H_2O\cdot C_2H_5OH$	17 240	20 490	25 970	3072	1608, 1593	1457, 1445	752	3.9

[a] There is also contribution from $\delta(NH_2)$ and ν(C=N) from the guanidine group.

[b] Calculated for the dinuclear compound.

3. Results and discussion

3.1. Synthesis and characterisation of the coordination compounds

Six coordination compounds with the benzimidazolic ligands: ntb, 2gb, bbimpy and 2pb Fig. 1, were synthesised and characterised by spectroscopic and analytical methods.

Two different synthetic routes were used for preparing the coordination compounds. In the first technique, chromium(III) is extracted, in anhydrous methanol or ethanol, from $CrCl_3$ by means of a Soxhlet and then reacted with the ligand, as previously reported for chelating ligands [23]. For the second method, a chromium(II) acidic aqueous solution is reacted with the ligand under oxygen-free conditions, followed by air oxidation [24]. The solution of chromium(II) is made from $CrCl_2$ or chromium metal in $HClO_4$ under a nitrogen atmosphere.

Compounds **1**, **5** and **6** can be prepared by either of these techniques, i.e. from Cr(II) or $CrCl_3$; however, yields are better when using the Soxhlet method.

The reactions with the 2gb ligand yielded two different types of chromium(III) compound, i.e. two mononuclear compounds **2** and **3**, and a dinuclear species **4**. The dinuclear compound is bridged by two hydroxo moieties and was obtained when a chromium(II) acid aqueous solution was reacted with a methanolic solution of 2gb. The coordination sphere of each chromium(III) contains two chelating 2gb molecules. It is known that the synthesis of the chromium(III) dinuclear species containing hydroxo bridges requires the addition of a base; however, in some instances this is not necessary, depending on the basicity of the ligand and the molar ratio of ligand to metal ion [16,17]. We here suggest that the basicity of 2gb is responsible for the formation of the hydroxo bridges. The same method of synthesis gave mononuclear species when ntb, bbimpy or 2pb were reacted with an acidic aqueous Cr(II) solution, indicating that they are less basic than 2gb.

Table 2 shows some of the main IR vibrational frequencies, UV–Vis absorption bands and magnetic moments.

3.2. Spectroscopy

The main vibrational frequencies observed for the benzimidazolic ring are those due to the ν(N–H), ν(C=C) + ν(C=N) vibrations, δ(N–H) and δ(C–H) benzimidazolic ring out of plane [8,10,25,26]. All the IR spectra of the coordination compounds show these vibrations, however in all cases the bands are shifted towards higher energy as compared with the position in the free ligand, Table 2. These results are indicative of ligand coordination through the imidazolic nitrogen. For the 2gb complexes the band due to $\nu(NH\cdots N)$ from the guanidine group in the ligand [8] is shifted from 3444 to 3300 cm^{-1} for **2** and **3**, and to 3341 cm^{-1} for **4**.

The strong band at 1317 (bbimpy) and 1314 cm^{-1} (2pb) in the spectra of the ligands is shifted towards higher energy and splitted upon chelation, indicating coordination through the pyridinic nitrogen [27,28]. The split band appears at 1321 and 1310 cm^{-1} for **5** and at 1323 and 1302 cm^{-1} for **6**. In the low-frequency infrared spectra of **1**, **5** and **6** the vibrational bands at 360, 343 and 361 cm^{-1}, respectively, were assigned as ν(Cr–Cl) [29], corroborating the presence of coordinated chlorides.

For Cr(III) hexacoordinated complexes there are three spin-allowed transitions in the electronic spectrum, ν_1 $^4T_{2g} \leftarrow {}^4A_{2g}$, ν_2 $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ and ν_3 $^4T_{1g}(P) \leftarrow {}^4A_{2g}$

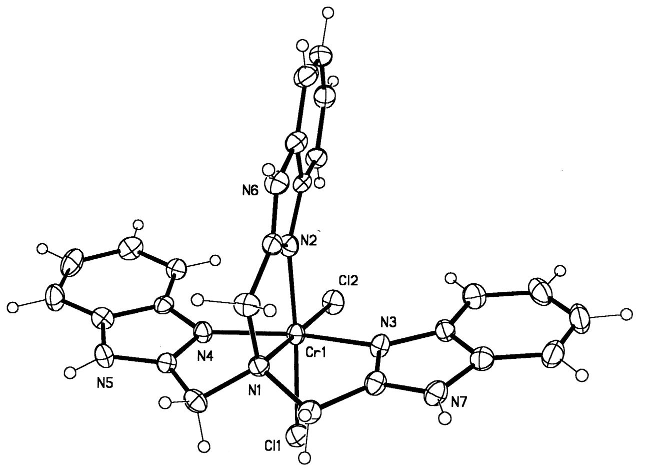


Fig. 2. Geometry for the cation $[CrCl_2ntb]^+$ in complex **1**. Thermal ellipsoids are at 50% probability level.

Table 3
Selected bond lengths (Å) and angles (°) with s.u. in parentheses for compound **1**

Cr1–N2	2.047(3)	Cr1–N4	2.050(3)
Cr1–N3	2.062(3)	Cr1–N1	2.154(3)
Cr1–Cl2	2.2909(13)	Cr1–Cl1	2.3180(13)
N2–Cr1–N4	88.26(13)	N2–Cr1–N3	87.82(13)
N4–Cr1–N3	157.18(14)	N2–Cr1–N1	82.95(13)
N4–Cr1–N1	78.30(13)	N3–Cr1–N1	78.91(13)
N2–Cr1–Cl2	95.75(10)	N4–Cr1–Cl2	103.23(10)
N3–Cr1–Cl2	99.52(10)	N1–Cr1–Cl2	177.98(10)
N2–Cr1–Cl1	172.76(11)	N4–Cr1–Cl1	89.30(10)
N3–Cr1–Cl1	91.80(10)	N1–Cr1–Cl1	89.88(10)
Cl2–Cr1–Cl1	91.45(5)		

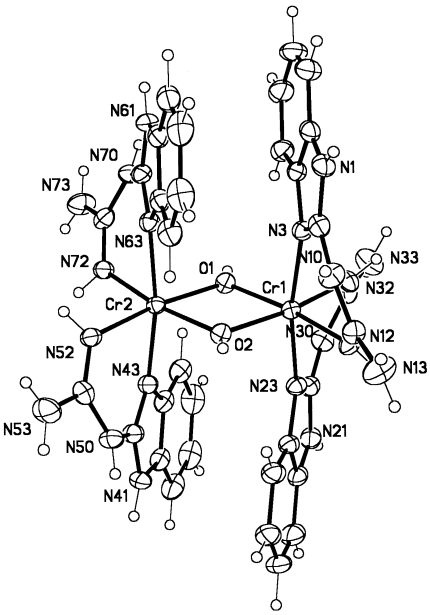


Fig. 3. Geometry for the cation $[Cr_2(2gb)_4(\mu\text{-}OH)_2]^{4+}$ in complex **4**. Thermal ellipsoids are at 30% probability level.

[30]. The diffuse reflectance spectra of compounds **1**–**6**, show three absorption bands, the first one in the region from 16 600 to 20 050 cm^{-1}, the second band from 20 000 to 25 400 cm^{-1} and the third from 25 000 to 36 100 cm^{-1}, where ν_1 correspond to 10 Dq for each complex (Table 2). The third band for compounds **1**, **3**, **4**, **5** and **6** appears as a shoulder obscured by CT bands. The electronic spectra of the compounds reported here are in reasonable agreement with those in the literature [30,31].

The magnetic moments at room temperature for compounds **1**, **2**, **3**, **5** and **6** correspond to the expected values for mononuclear chromium(III) compounds. Compound **4** has a magnetic moment at room temperature of 4.96 MB, smaller than the expected value (5.43 MB spin only) for a Cr(III) dinuclear species [32]. Studies of the variable temperature magnetic susceptibility of **4** were made at 3500 Oe and in the temperature range 17–280.15 K. Least-squares analysis was used to fit the data to a susceptibility expression based on the isotropic spin Hamiltonian [33]:

$$H = -2J(S_1 \cdot S_2)$$

The best fit of the susceptibility data reveals that the dinuclear compound has weak antiferromagnetic coupling ($J = -2.05$ cm^{-1}). This value is within the range of those for other dinuclear di-μ-hydroxo-chromium(III) complexes [17].

3.3. Description of the structures

3.3.1. Complex 1

The cation $[CrCl_2ntb]^+$ is depicted in Fig. 2. Ntb acts as a tetradentate ligand coordinating through the amine N atom and the three benzimidazole N atoms to the metal ion, as reported for a number of ntb complexes [2]. Two Cl atoms in a *cis* configuration complete the coordination sphere, yielding an hexacoordinated arrangement for the metal. It should be mentioned that only two related ntb-containing complexes with an hexacoordinated metal environment have been reported up to now, with Fe(II) [34] and Ni(II) [9]. On the other hand, **1** is the first reported X-ray characterised Cr(III)–ntb complex.

As expected, the tertiary N atom presents a bond length about 0.10 Å longer than those for the benzimidazole N atoms (see Table 3). The tripodal ntb ligand is forced to adopt a planar geometry in order to retain the octahedral geometry on the metal–dihedral angle between the aromatic moieties containing the rings [N3, N7] and [N4, N5] is 10.1°, while angles of these planes with the third moiety [N2, N6] are 89.6 and 79.6°. This uncommon spatial arrangement for ntb reflects the great versatility of this tripodal ligand in order to take in the preferred geometry of the metal ion. On the other

Table 4
Selected bond lengths (Å) and angles (°) for compound **4**

Cr1–O2	1.960(3)	Cr1–O1	1.961(3)
Cr1–N12	2.021(3)	Cr1–N32	2.023(4)
Cr1–N3	2.045(3)	Cr1–N23	2.052(3)
Cr2–O1	1.953(3)	Cr2–O2	1.955(3)
Cr2–N72	2.019(3)	Cr2–N52	2.020(4)
Cr2–N63	2.056(3)	Cr2–N43	2.060(3)
O2–Cr1–O1	75.83(11)	O2–Cr1–N12	92.50(14)
O1–Cr1–N12	168.30(14)	O2–Cr1–N32	168.65(13)
O1–Cr1–N32	92.86(13)	N12–Cr1–N32	98.82(15)
O2–Cr1–N3	93.25(13)	O1–Cr1–N3	95.54(13)
N12–Cr1–N3	84.10(14)	N32–Cr1–N3	88.72(14)
O2–Cr1–N23	95.31(13)	O1–Cr1–N23	92.78(13)
N12–Cr1–N23	89.10(14)	N32–Cr1–N23	84.14(14)
N3–Cr1–N23	169.29(14)		
O1–Cr2–O2	76.12(11)	O1–Cr2–N72	93.49(14)
O2–Cr2–N72	169.49(14)	O1–Cr2–N52	169.32(14)
O2–Cr2–N52	93.30(14)	N72–Cr2–N52	97.13(15)
O1–Cr2–N63	92.25(13)	O2–Cr2–N63	94.87(13)
N72–Cr2–N63	83.81(14)	N52–Cr2–N63	90.01(14)
O1–Cr2–N43	95.06(13)	O2–Cr2–N43	92.23(13)
N72–Cr2–N43	90.25(14)	N52–Cr2–N43	83.82(14)
N63–Cr2–N43	170.85(14)		
Cr2–O1–Cr1	104.03(12)	Cr2–O2–Cr1	104.01(12)

hand, the Cr ion lies in the plane formed by N1, N3, N4 and Cl2 (calculated maximal deviation: 0.025 Å). As a result of these features, the deviations from an ideal octahedral geometry around the Cr ion are the following: *trans* angles range from 157.18(14) to 177.98(10)° and *cis* angles from 78.30(13) to 99.52(10)°.

Ethanol and water molecules included in the cell form a complex tri-dimensional network of hydrogen bonds using benzimidazolic N atoms and chlorine atoms as acceptors (H···A separations in the range 1.854–2.468 Å), which probably greatly stabilises the crystal.

3.3.2. Complex 4

Complex **4** is the first X-ray characterised Cr(III) complex including 2gb as ligand. The dinuclear cation $[Cr_2(2gb)_4(\mu\text{-OH})_2]^{4+}$ is depicted in Fig. 3. It should be mentioned that the charge of the cation is in line with the four ClO_4^- anions present in the asymmetric unit and with the fact that the H atoms of the OH groups were found on difference Fourier maps. The $(\mu\text{-OH})_2$ bridge is symmetric, with Cr–O bond lengths in the range 1.953(3)–1.961(3) Å. The metal–metal separation, 3.085 Å, is similar to that reported for other complexes containing the $Cr_2(\mu\text{-OH})_2$ fragment, as well as the Cr–O–Cr angles, 104.02° [35–38] (Table 4). Each Cr(III) ion coordinates two 2gb ligands with Cr–N bond lengths in the short range 2.019(3)–2.060(3) Å, as expected. For each ligand, the N atom bonded to the benzimidazolic moiety lies in the plane of the imidazole: deviations for N10, N30, N50 and N70 from the mean planes formed by the benzimidazolic groups are in the range 0.040–0.048 Å. This point confirms that the coordinated 2gb ligand in **4** is the same as the free ligand depicted in Fig. 1. However, deviations from an ideal octahedral geometry are smaller than in the case of **1**, because 2gb acts as a bidentate ligand while ntb is tetradentate: *cis* and *trans* angles for Cr1 are from 75.83(11) to 95.54(13)° and from 168.30(14) to 169.29(14)°, respectively, and ranges are similar for Cr2. This distortion is reflected in the dihedral angles between the benzimidazolic rings for two 2gb coordinated on the same metal centre: 29.0° between planes [N1, N3] and [N21, N23] and 29.6° between planes [N41, N43] and [N61, N63]. In spite of the parallel arrangement of the benzimidazolic rings in the complex, no intramolecular interactions are observed: the shortest calculated separation between the centroids of the benzene rings is 4.13 Å.

As in the previous case, numerous hydrogen bonds which involve five water molecules, μ-OH groups, NH of imidazole, NH and NH_2 of 2gb stabilise, the crystals (H···A separations from 1.971 to 2.624 Å).

4. Supplementary data

Supplementary data are available from the CCDC on request, quoting the deposition numbers CCDC 140724 (**1**) and 140725 (**4**). The information can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] J. Reedijk, Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987 (Chapter 13.2).

[2] R. Rajan, R. Rajaram, B.U. Nair, T. Ramasami, S.K. Mandal, J. Chem. Soc., Dalton Trans. (1996) 2019.

[3] J. García-Lozano, J. Server-Carrió, E. Coret, J.-V. Folgado, E. Escrivà, R. Ballesteros, Inorg. Chim. Acta 245 (1996) 75.

[4] T.J. Cardwell, A.J. Edwards, J.M. Hartshorn, R.J. Holmes, W.D. McFadyen, Aust. J. Chem. 50 (1997) 1009.

[5] R.W. Gable, R.M. Hartshorn, W.D. McFadyen, L. Nunno, Aust. J. Chem. 49 (1996) 625.

[6] C. Piguet, B. Bocquet, E. Müller, A.F. Williams, Helv. Chim. Acta 72 (1989) 323.

[7] T.M. Aminabhavi, N.S. Biradar, S.B. Patil, D.E. Hoffman, Inorg. Chim. Acta 125 (1986) 125.

[8] N. Barba-Behrens, A. Vázquez-Olmos, S.E. Castillo-Blum, G. Höjer, S. Meza- Höjer, R.M. Hernández, M.J. Rosales-Hoz, R. Vicente, A. Escuer, Transition Met. Chem. 21 (1996) 31.

[9] M.E. Quiroz-Castro, H. Nöth, S. Bernès, N. Barba-Behrens, Polyhedron 19 (2000) 1479.

[10] S. Wang, S. Yu, Q. Luo, Q. Wang, J. Shi, Q. Wu, Transition Met. Chem. 19 (1994) 205.

[11] J. Chatlas, S. Kaizaki, E. Kita, P. Kita, N. Sakagami, R. van Eldik, J. Chem. Soc., Dalton Trans. (1999) 91, and references therein.

[12] J.A. Winter, D. Caruso, R.E. Shepherd, Inorg. Chem. 27 (1988) 1086.

[13] J.R. Bocarsly, M.Y. Chiang, L. Bryant, J.K. Barton, Inorg. Chem. 29 (1990) 4898.

[14] H. Bhushan, L.K. Mishra, Ind. J. Chem. 21A (1982) 1135.

[15] A. Mishra, J.P. Singh, J. Ind. Chem. Soc. 56 (1979) 771.

[16] S.J. Brudenell, S.J. Crimp, J.K.E. Higgs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chim. Acta 247 (1996) 35.

[17] L. Spiccia, G.D. Fallon, A. Markiewicz, K.S. Murray, H. Riesen, Inorg. Chem. 31 (1992) 1066, and references therein.

[18] A.E. Ceniceros-Gómez, N. Barba-Behrens, S. Bernès, H. Nöth, S.E. Castillo-Blum, Inorg. Chim. Acta 304 (2000) 230.

[19] A.E. Ceniceros-Gómez, A. Ramos-Organillo, J. Hernández-Díaz, J. Nieto-Martínez, R. Contreras, S.E. Castillo-Blum, Heteroatom. Chem. (2000), in press.

[20] SADABS, Siemens Area Detector Absorption Corrections, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA.

[21] G.M. Sheldrick, SHELXTL-plus, release 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1995.

[22] G.M. Sheldrick, SHELX-97 Users Manual, University of Göttingen, Germany, 1997.

[23] V. Ugalde-Saldivar, M.A. Luna-Canut, M.E. Sosa-Torres, M.J. Rosales-Hoz, R.A. Toscano, M.L. Tobe. J. Chem. Soc., Dalton Trans. (1990) 3629.

[24] C.S. Lee, E.M. Gorton, H.M. Neumann, H.R. Hunt, Inorg. Chem. 5 (1966) 1397.

[25] L.K. Thompson, B.S. Ramaswamy, E.A. Seymour, Can. J. Chem. 55 (1977) 878.

[26] T.J. Lane, I. Nakagawa, J.L. Walter, J. Kandathil, Inorg. Chem. 1 (1962) 267.

[27] J.R. Sams, T.B. Tsin, J. Chem. Soc., Dalton Trans. (1976) 488.

[28] T.A. Kabanos, A.D. Keramidas, D. Mentzafos, U. Russo, A. Terzis, J.M. Tsangaris. J. Chem. Soc., Dalton Trans. (1992) 2729.

[29] J.R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York, 1971, pp. 111–183.

[30] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, Amsterdam, 1984.

[31] D.J. Hodgson, M.H. Zietlow, E. Pedersen, H. Toflund, Inorg. Chim. Acta 149 (1988) 111.

[32] C.J. O'Connor, Prog. Inorg. Chem. 29 (1982) 203.

[33] T. Fujihara, A. Fuyuhiro, S. Kaizaki. J. Chem. Soc., Dalton Trans. (1995) 1813.

[34] S. Wang, Q. Luo, X. Wang, L. Wang, K. Yu. J. Chem. Soc., Dalton Trans. (1995) 2045.

[35] H.R. Fischer, D.J. Hodgson, K. Michelsen, E. Pedersen, Inorg. Chim. Acta 88 (1984) 143.

[36] M.A. Heinrichs, D.J. Hodgson, K. Michelsen, E. Pedersen, Inorg. Chem. 23 (1984) 3174.

[37] M. Ardon, A. Bino, K. Michelsen, J. Am. Chem. Soc. 109 (1987) 1986.

[38] B.G. Gafford, R.A. Holwerda, Inorg. Chem. 28 (1989) 60.