Synthesis and Characterization of Novel Binuclear Chromium(III) Complexes bridged by Aromatic Heterocyclic Compounds

Manabu Nakahanada, Kazuhito Ino and Sumio Kaizaki *
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

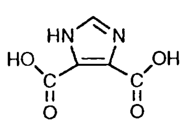
Two novel types of binuclear bis(acetylacetonato)chromium(III) complexes bridged by imidazole-4,5-dicarboxylate, 1,2,3-triazole-4,5-dicarboxylate and pyrazole-3,5-dicarboxylate and a binuclear complex bridged by both pyrazolate and hydroxide ligands were prepared and characterized by elemental analysis and positive-ion fast atom bombardment mass spectrometry. Their spectroscopic and magnetic properties were examined by means of luminescence, ^{2}H NMR and magnetic susceptibility measurements.

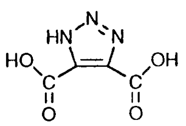
In contrast to the large number of investigations on edge-sharing binuclear transition-metal complexes with two OR^- bridges (R = H, Me, Et or *p*-substituted phenyl),[1-3] there have been few on binuclear complexes bridged by tetradentate ligands such as disubstituted aromatic heterocyclics, other than copper(II) complexes.[4-10] In the case of chromium(III), the interaction of the π electrons of the heterocycle with the magnetic t_{2g} (d_π) orbitals of the complex is expected to reveal new aspects of the magnetic interaction in comparison to copper(II) complexes having magnetic e_g (d_σ) orbitals. It is interesting to examine the contribution to the spectroscopic properties and magnetic interaction from the ring isomers of π-excessive five-membered heterocyclic π donors[11] in binuclear complexes, where the numbers of intervening bonds between the two metal atoms differ.

In this paper, we report the syntheses and characterization of two novel types of binuclear bis(acetylacetonato)chromium(III) complexes bridged by dicarboxylate derivatives of five-membered aromatic nitrogen heterocyclic compounds, imidazole-4,5-dicarboxylate (imdc^{3-}), 1,2,3-triazole-4,5-dicarboxylate (tzdc^{3-}) and pyrazole-3,5-dicarboxylate (pzdc^{3-}), a binuclear complex bridged by both pyrazolate (pz$^-$) and hydroxide and a mononuclear chromium(III) complex with 4-methylimidazole-5-carboxylate (mimc$^-$).

Experimental

Preparation of Complexes.—$Na[Cr_2(acac)_4(\mu\text{-}L)]\cdot nH_2O$ (L = imdc^{3-} **1**, tzdc^{3-} **2** *or* pzdc^{3-} **3**). A mixture of *trans*-$[Cr(acac)_2(H_2O)_2]Cl$[12] (1.00 g, 3.1 mmol), H_3L (1.5 mmol) and sodium carbonate (0.24 g, 2.3 mmol) in water (40 cm^3) was heated at 60 °C on a water-bath. The colour changed from red to red-purple with slow evolution of carbon dioxide. After 1 h the mixture was cooled to room temperature, diluted and then poured onto a column (4 × 20 cm) of QAE-Sephadex A-25 anion exchanger. The column was washed with water and eluted with 0.05 mol dm^{-3} NaCl solution. Two bands (I and II in elution order) were obtained, the former in much greater volume. Each eluate was concentrated to dryness on a vacuum rotary evaporator at 30 °C. The resulting solids were dissolved in methanol and acetone, and sodium chloride was filtered off. After this procedure was repeated a few times the pure complexes were obtained as fine red-purple crystals for **1** and **2**, and as fine violet crystals for **3** by recrystallization from water. The crystals were filtered off, washed a few times with a small amount of ice-cold water, and dried *in vacuo*. The yield of each complex was about 20%.


H_3imdc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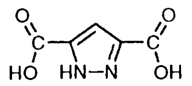
H_3pzdc

The second band II only for complex **3** was isolated and purified as above.

$[Cr_2(acac)_4(\mu\text{-}pz)(\mu\text{-}OH)]\cdot H_2O$ **4**. A mixture of *trans*-$[Cr(acac)_2(H_2O)_2]Cl$ (1.0 g, 3.1 mmol), Hpz (0.21 g, 3.0 mmol) and sodium carbonate (0.16 g, 1.5 mmol) in water (10 cm^3) was warmed at 60 °C on a water-bath. The colour changed from red to red-purple. A pink powder was gradually formed after 30 min. After further warming for 2 h the pink powder was filtered off, washed with ice-cold water, and dried *in vacuo*. The yield was about 10%.

$Na[Cr_2(acac)_4\{\mu\text{-}[2\text{-}^2H]imdc\}]$ **1d**. Imidazole-4,5-dicarboxylic acid was deuteriated by the following modified method for imidazole:[13] H_3imdc (0.08 g, 0.5 mmol) and sodium hydroxide (0.06 g, 1.5 mmol) were dissolved in D_2O (3 cm^3), and refluxed for 2 d. To the cooled solution, *trans*-$[Cr(acac)_2(H_2O)_2]Cl$ (0.33 g, 1.0 mmol) in water (10 cm^3) was added. The mixture was neutralized with a small amount of dilute hydrochloric acid solution. The deuteriated complex was separated and purified as above. The yield was about 20%.

$[Cr(acac)_2(mimc)]\cdot 3H_2O$ **5**. Ethyl 4-methylimidazole-5-carboxylate (0.39 g, 2.5 mmol) was dissolved in boiling ethanol–water–sodium hydroxide (10 cm^3, 10 cm^3, 1.0 g). The mixture was kept boiling for 10 min to hydrolyse the ester. Ethanol was evaporated and the colour of the solution became brown. After neutralization with dilute hydrochloric acid solution, *trans*-$[Cr(acac)_2(H_2O)_2]Cl$ (0.66 g, 2.0 mmol) was added. The mixture was filtered and the filtrate allowed to stand overnight at room temperature. A red-purple precipitate was deposited in high yield. This was filtered off, washed with ice-cold water and dried *in vacuo*.

$[Cr(acac)_2\{[2\text{-}^2H]mimc\}]$ **5d**. In order to obtain deuteriated mimc, the hydrolysis of ethyl 4-methylimidazole-5-carboxylate

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Non-SI units employed: emu = $10^6/4\pi$SI, $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

was carried out with deuterium oxide by same method described above. The mixture was kept refluxing for 1 d. The deuteriated complex was obtained in good yield by the method described above.

Measurements.—Absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer, ^2H NMR spectra on a JEOL JNM GSX-270 spectrometer at room temperature. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102 mass spectrometer in methanol. Luminescence spectra were measured for KBr disks on a JASCO R-800 laser Raman spectrophotometer at 85 K cooled with liquid nitrogen and equipped with a NEC GLS 3200 argon-gas laser. High-performance liquid chromatography (HPLC) was performed by using a JASCO 807-IT integrator, BIP-I HPLC pump and 875 UV/VIS detector. The Chiralpack OT(+) column was eluted with hexane–propan-2-ol (1:1). Infrared spectra were obtained as KBr disks on a Shimadzu IR-435 spectrophotometer at room temperature, CD spectra on a JASCO J-500C spectropolarimeter.

The concentration of the chromium(III) complexes was determined spectroscopically after oxidation in alkaline hydrogen peroxide solution, using the molar absorption of chromate(VI) ion (ε = 4830 dm^3 mol^{-1} cm^{-1}) at 372 nm.

Magnetic susceptibility data were obtained on powdered samples by using an automated Faraday balance in the temperature range 80–295 K. The observed susceptibilities were fitted by the theoretical expression by means of a non-linear least-squares SIMPLEX parameter-optimization routine, minimizing the residual function $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/(\chi_{obs})^2]^{\frac{1}{2}}$.

Results and Discussion

General Characterization.—From the positions of the first ligand-field absorption band (Table 1), complexes **1**–**5** are considered to have a $CrNO_5$-type chromophore. Complexes **1**–**3** seem to have an uninegative charge in view of the column chromatographic behaviour. The elemental analyses (Table 2) show that the ratio of Cr:L^{3-} is 2:1. Complexes **4** and **5** seem to be neutral with a binuclear structure bridged by pyrazolate and hydroxide, and mononuclear respectively, from the elemental analysis (Table 2) and low solubility in water. The FAB mass spectra are in accord with these conclusions.

The selected positive-ion FAB mass spectral data measured in methanol solution are summarized in Tables 3 and 4. For complexes **1** and **3** having the same molecular weight many peaks are observed at the same *m*/*z* values; for example, three types of quasi-molecular-ion peaks ($[M + Na]^+$, *m*/*z* 699; $[M + H]^+$, 677; $[M + 2H - Na]^+$, 655), a fragment-ion peak corresponding to loss of acetylacetonate anion ($[M - acac]^+$, *m*/*z* 577) and a peak for an associated molecule ($[2M + Na]^+$, *m*/*z* 1375), as shown in Table 3. These experimental data indicate that each heterocyclic compound in **1**–**3** co-ordinates to two chromium(III) ions as a tetradentate trinegative ligand forming five-membered N–O chelate rings as shown in Fig. 1.

For complex **4**, a weak quasi-molecular ion peak ($[M + H]^+$, *m*/*z* 585) is also observed. Since this complex is neutral, no cation source like Na^+ or H^+ exists in methanol solution. This seems to be the reason why the intensity of this quasi-molecular ion peak is weak and that the peak intensity increases upon loss of bridging ligand (pz^- or OH^-) or acetylacetonate. Stronger peaks than the quasi-molecular peak upon loss of one uninegative acetylacetonate or bridging ligand are often observed for neutral binuclear chromium(III) complexes.[3] The composition of the signal at *m*/*z* = 517 seems to be $[M + H - Hpz]^+$ or $[M - pz]^+$, formed by loss of Hpz from the quasi-molecular ion. Both the *m*/*z* value and unipositive charge of this peak support the fact that the bridging aromatic heterocyclic compound is deprotonated. Therefore, complex **4** is considered to adopt a binuclear structure bridged by a pz^- and a hydroxide ligand.

The present FAB mass spectra are also a useful method for determining molecular weights of acac complexes, as was proposed for acetylacetonate[3,14] and edta(ethylenediaminetetraacetate) complexes.[15]

Stereochemistry of the Binuclear Complex.—There are two possible isomers, *i.e. meso* and racemic forms, of these bis(bischelate) binuclear complexes. For the imdc complex there is no steric interaction between the two acac chelates since the two chromium(III) moieties are obviously separated from each other as shown in Fig. 1. Though no indication of separation of racemic and *meso* isomers was found by chromatography, complex **2** seems to be a mixture of such isomers. On the contrary, the racemic isomer of the pzdc binuclear complex may be more stable than the *meso* one, since the latter has more steric crowding between the two acac chelate rings according to molecular model considerations, as seen in Fig. 1.

The HPLC of complex **3** (band I) gave one broad band. The earlier and later parts of the eluate gave large CD bands in the intraligand transition region near 324 nm for the acetylacetonate ligand, as observed for bis(acac) complexes.[4,16] These CD patterns are enantiomeric, as observed upon optical resolution of the ΔL and ΛL diastereoisomers of $[Cr(acac)_2(O^2,O^3\text{-L-Htart})]^{2-}$ (H_2tart = tartaric acid).[14] In view of this CD behaviour, it is evident that complex **3** (band I) adopts a racemic structure of ($\Delta\Delta$ and $\Lambda\Lambda$) with respect to the configurational chirality around each metal ion.[16] It is plausible that the isomer formed in higher yield adopts the more stable racemic structure.

Only from complex **3**, was a second band (II) isolated as a pure solid. Its amount was smaller than that of band I, but the ratio of I:II was much larger than that for **1** and **2**. Band I is

Table 1 Selected absorption spectral data in methanol [$\sigma_{max}/10^3$ cm^{-1} (log ε/dm^3 mol^{-1} cm^{-1})]

Complex				
1	2	3	4	5
14.7 (0.60)		14.7 (0.81)		
18.4 (2.17)	18.2 (2.18)	17.9 (2.11)	18.2 (1.98)	18.2 (1.87)
26.2 (2.79)	25.6 (2.79)	25.5 (2.89)	26.2 (2.70)	25.6 (2.54)
30.2 (4.38)	30.0 (4.28)	29.7 (4.34)	30.7 (4.32)	30.0 (4.07)
38.8 (4.42)	38.9 (4.18)	38.9 (4.36)	39.4 (4.24)	39.4 (3.99)

Table 2 Elemental analytical data with calculated values in parentheses

	Analysis (%)			
Complex	C	H	N	Cr
1 $Na[Cr_2(acac)_4(imdc)]\cdot 3H_2O$	40.95 (41.10)	4.85 (4.85)	3.75 (3.85)	14.30 (14.25)
2 $Na[Cr_2(acac)_4(tzdc)]\cdot 5H_2O$	38.15 (37.55)	5.05 (5.00)	5.40 (5.45)	13.55 (13.55)
3 (I) $Na[Cr_2(acac)_4(pzdc)]\cdot 4.5H_2O$	39.90 (39.65)	5.05 (5.05)	3.70 (3.70)	
3 (II) $Na[Cr_2(acac)_4(pzdc)]\cdot 4.5H_2O$	39.35 (39.65)	5.10 (5.05)	3.80 (3.70)	
4 $[Cr_2(acac)_4(pz)(OH)]\cdot H_2O$	45.20 (45.85)	5.55 (5.70)	4.60 (4.65)	17.70 (17.25)
5 $[Cr(acac)_2(mimc)]\cdot 3H_2O$	41.60 (41.95)	5.80 (5.85)	6.40 (6.50)	12.20 (12.10)

violet and II is red-purple on QAE-Sephadex chromatography. Since the elemental analysis (Table 2), mass (Table 3) and IR spectra of band II are almost identical with those of band I, the former can be assumed to adopt a similar binuclear structure to that of the latter. Species II seems to adopt a *meso* form, which is stable on the column but may isomerize to a racemic form during recrystallization, in view of the observation of the same CD behaviour upon HPLC resolution.

Luminescence Spectra.—The luminescence data for the five complexes are compared in Table 5 with those of [Cr(acac)$_2$(glyO)][17] **6** [glyO = glycinate(1 –)] of CrNO$_5$ type where the nitrogen donor of glycinate has no π electrons. The luminescence peak of **5** is observed at lower energy than that of **6**. This shift results from the increasing covalency due to the π orbitals of imidazolate in **5**; and decreasing (nephelauxetic effect) Racah interelectron repulsion parameter *B*.[18] On the other hand, for the binuclear complex **1** which also contains an imidazolate moiety the emission peak is shifted to lower energy than that of the mononuclear complex **5**. The peaks of complexes **2** and **3** are also observed at lower energies. These lower-energy shifts of the lowest excited ^2E_g state seem to arise from the following causes. First is the deprotonation of the imidazolate or triazolate and/or pyrazolate derivatives, strengthening the π-donor properties toward chromium(III) and increasing the covalency effect. Secondly is the magnetic spin–spin interaction, resulting in moderately large splittings for the excited and/or ground states of the chromium(III) complexes. In view of the fact that the ground-state spin–spin coupling is too small for one to differentiate the transition energies by means of room-temperature measurements, interactions such as $^4A_2$–^2E may be more appreciable in the excited than in the ground state. This seems to be responsible for the shift of the luminescence to lower energy.

^2H NMR Spectra.—The ^{2}H NMR spectra of complexes **1** and **5** in dimethylformamide solution give contact shifts at high field as observed for the mononuclear imidazole complex [Cr(nta){[1,2-$^2H_2$]Him}$_2$] (nta = nitrilotriacetate).[13] The shift (δ −73.9) for the deuteron at the 2 position of the bidentate imidazole-4,5-dicarboxylate in **1** is about twice as large as that (δ −46.8) for the 2-deuteron of the mimc in the mononuclear complex **5**. This situation is similar to the case of an acetate-bridged binuclear complex where the methyl deuterons in the bridging ligand are influenced by two chromium(III) ions.[19]

Magnetic Properties.—The temperature-dependent magnetic susceptibility data for complexes **1**–**3** were fitted by the well known Van Vleck equation (1) where *J* and *j* are defined by the exchange Heisenberg Hamiltonian expressed as $H = 2JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$. The results are summarized in Table 6. The biquadratic exchange parameter *j* is insignificantly small. Plots of χ *vs.* *T* are shown in Fig. 2. Little difference in the coupling constants is observed between complexes **1** and **2** having the same bridging structure, indicating that the magnetic interaction does not depend on the number of nitrogen atoms in the heterocycle (imidazolate and triazolate).

Complex **3** shows a weak ferromagnetic interaction (Table 6), whereas a copper(II) binuclear complex bridged by two pyrazolate derivatives exhibits a large antiferromagnetic interaction.[10] The difference in the magnetic interaction between these two complexes depends on the properties of the magnetic orbitals which are $e_g(d_\sigma)$ and $t_{2g}(d_\pi)$ for copper(II) and chromium(III), respectively.

Though complexes **1** and **3** have the same composition, their magnetic interactions are different, being antiferromagnetic and weakly ferromagnetic, respectively. The magnitude of the interaction in **3** (|2*J*| value) is smaller than that of **1** which has a

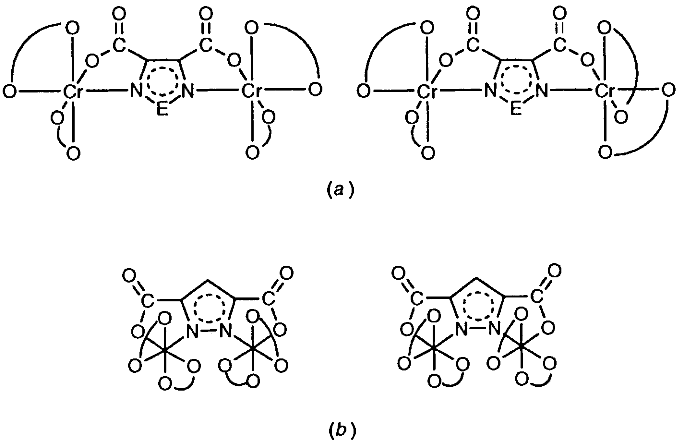

Fig. 1 Proposed structure for (*a*) *meso* (left) and racemic (right) [Cr$_2$(acac)$_4$(imdc)]$^-$ (E = C) and [Cr$_2$(acac)$_4$(tzdc)]$^-$ (E = N), (*b*) the *meso* (left, species II) and racemic (right, species I) isomers of [Cr$_2$(acac)$_4$(pzdc)]$^-$ **3**

Table 3 Selected FAB mass spectral data for complexes **1** and **3**

	Relative intensity (%)			
m/*z*	**1**	**3** (I)	**3** (II)	Assignment
1375	25	10		[2*M* + Na]$^+$
926	10	10		[*M* + Cr(acac)$_2$]$^+$
699	40	80		[*M* + Na]
677	50	20	20	[*M* + H]$^+$
655	10	10	30	[*M* + 2H −Na]$^+$
600	35	25		[*M* + Na − acac]$^+$
577	55	35	10	[*M*-acac]$^+$
250	100	100	100	[Cr(acac)$_2$]$^+$

M = 676 for Na[Cr$_2$(acac)$_4$(imdc)] and Na[Cr$_2$(acac)$_4$(pzdc)].

Table 4 Selected FAB mass spectral data for complexes **2**, **4** and **5**

2			**4**			**5**		
m/*z*	Relative intensity (%)	Assignment	*m*/*z*	Relative intensity (%)	Assignment	*m*/*z*	Relative intensity (%)	Assignment
1377	2	[2*M* + Na]$^+$	585	10	[*M* + H]$^+$	625	20	[*M* + Cr(acac)$_2$]$^+$
700	15	[*M* + Na]$^+$	567	60	[*M* − OH]$^+$	526	15	[*M* + Cr(acac)]$^+$
678	15	[*M* + H]$^+$	517	30	[*M* − pz]$^+$	376	70	[*M* + H]$^+$
601	10	[*M* + Na − acac]$^+$	485	100	[*M* − acac]$^+$	276	20	[*M* − acac]$^+$
578	10	[*M* − acac]$^+$	417	100	[*M* − pz − Hacac]$^+$	250	100	[Cr(acac)$_2$]$^+$
250	100	[Cr(acac)$_2$]$^+$	385	40	[*M* − acac − Hacac]$^+$			
			250	60	[Cr(acac)$_2$]$^+$			

M = 677 for Na[Cr$_2$(acac)$_4$(tzdc)] **2**; 584 for [Cr$_2$(acac)$_4$(pz)(OH)] **4** and 375 for [Cr(acac)$_2$(mimc)] **5**.

$$\chi = \frac{Ng^2\mu\beta}{kT} \times \frac{2\exp[(2J - 6.5j)/kT] + 10\exp[(6J - 13.5j)/kT] + 28\exp[(12J - 9j)/kT]}{1 + 3\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j)/kT] + 7\exp[(12J - 9j)/kT]} \quad (1)$$

Table 5 Luminescence spectral data

Complex	$\sigma_{max}/10^3$ cm^{-1}
1	12.25
2	12.09
3	12.20
4	12.45, 13.80
5	12.37
6	12.50, 12.99

Table 6 Magnetic properties

			μ_{eff}/μ_B [b]	
Complex	$2J$[a]/cm^{-1}	g	295 K	100 K
1	−5.41	2.05	3.92	3.80
2	−7.08	1.98	3.76	3.60
3	+0.83	2.04	3.93	4.01
4	−4.90	2.09	3.98	3.80

[a] Refers to the coupling constant determined from the observed magnetic susceptibility data. [b] Magnetic moment per chromium(III) ion.

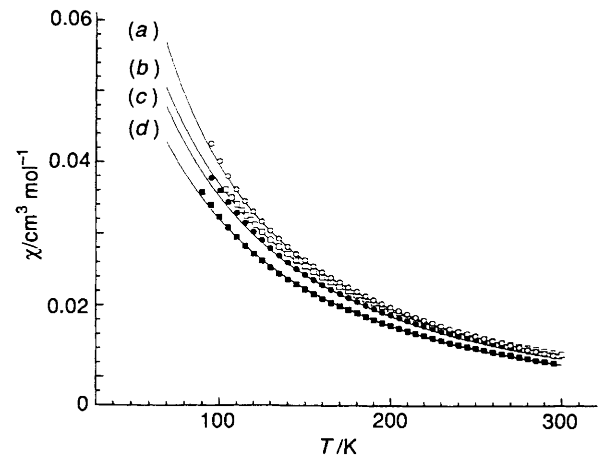

Fig. 2 Temperature-dependent magnetic susceptibilities of complexes **3** (*a*) **4** (*b*) **1** (*c*) and **2** (*d*). The full lines represent the best fit using the Van Vleck equation ($S = \frac{3}{2}, \frac{3}{2}$)

longer metal–metal distance. The sign of the magnetic couplings could be predicted through an analogous approach to spin transfer in NMR spectroscopy.[20] Taking into account the π highest occupied molecular orbital for imidazole[21] and pyrazole[22] where the nodal plane is located at the C(1)–N(5) and C(4)–N(3) bonds and at the C(3)–N(2) and C(5)–N(1) bonds, respectively, an in-phase d_π–p_π–d_π interaction is expected and leads to an antiferromagnetic interaction for complexes **3** and **4** through the π path, even though the number of intervening bonds for **2** is different from that for **3**. On the other hand, the σ path results in ferromagnetic and antiferromagnetic interaction for the binuclear complexes **1** and **3**, respectively, depending on the numbers of intervening bonds. In **1**, the π path overcomes the σ one. For **3** another mechanism such as direct d_{z^2}–d_{xy}[23] and/or d_{yz}–d_{yz} or d_{yz}–d_{xy} (*via* the π orbital of the bridging pyrazolate)[24] orthogonal coupling leading to a ferromagnetic interaction should be considered. Complex **4** bridged by pyrazolate and hydroxide shows an antiferromagnetic interaction, suggesting that the ferromagnetic interaction through the pz bridge is masked by the antiferromagnetic one through the hydroxide bridge.

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