Preparation of a novel *cis* isomer of bis(malonato)chromate(III) type complexes

Sumio Kaizaki*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560 (Japan)
Naoko Hirota, Kayoko Segawa, Mieko Tanabe, Atsuko Okumura, Mika Yamamoto
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630 (Japan)
and J. Ivan Legg**
Department of Chemistry, Washington State University, Pullman, WA 99164-4630 (USA)

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Abstract

In the course of the preparation of *cis*-bis(malonato)chromate(III) complexes with pyridine, ethylenediamine, *N,N*-dimethylethylenediamine, 2-aminomethylpyridine, glycinate, oxalate and acetylacetonate, another type of *cis* isomer was found during QAE-Sephadex column chromatography. Most of them were isolated and characterized in terms of elemental analyses, absorption, and ^{2}H NMR spectra. Their spectroscopic behaviors were compared.

Introduction

It is well known that the coordination theory for octahedral six-coordinate complexes was founded on the basis of the number of geometrical isomers of $[CoX_2(N)_4]$ and $[CoXY(N)_4]$ type complexes by Alfred Werner. Since then, it is obvious that there has been no exception for such a criterion of typical Werner type complexes, other than counting the number of conformational isomers (diastereomers) or linkage isomers with respect to the chelate conformations or kinds of ligating atoms [1]. For the malonate chelate ring, there are a few possible conformations which have been found in crystals by X-ray analyses [2]. However, there has been no report on the isolable conformational isomers with each possible chelate conformation, since they seem to be too flexible to exist in solution. Another possibility is a quasi-isomer because of deprotonation of the malonate methylene as found in the macrocyclic tetramine(malonato)chromium(III) complex [3]. This may be rejected by taking account of the charges of the complexes.

In this article, we report the syntheses of two isomers of the *cis* type for the bis(malonato)chromate(III) complexes and compare their absorption and ^{2}H NMR spectra, leading to the substantiation of the paradoxical existence of unprecedented isomerism, which might seemingly question Werner's paradigm for the coordination theory of octahedral six-coordinate complexes.

Experimental

Preparation of pyridine complexes

Seven grams of *cis*-$Na[Cr(mal)_2(H_2O)_2]\cdot 3H_2O$ were dissolved in 7 cm^3 of water. To this solution was added 7 cm^3 of pyridine. The resulting blue–violet solution was heated on a steam bath at 80 °C for 3 h. The color of the solution changed from blue–violet to red–violet. The excess pyridine in this reaction solution was extracted with ether as follows. After a mixture of the solution and ether in equal volumes was stirred for a while, the ether was decanted, and the procedure was repeated several times. The red precipitate obtained in the aqueous-pyridine phase was collected by filtration and recrystallized from water and acetone. A half volume of the filtrate from the reaction solution was poured onto a column (4.5×55 cm) of QAE-Sephadex anion exchanger(Cl^- form). After the column was washed with water, the adsorbed band was eluted with 0.05 M (1 M=1 mol dm^{-3}) LiCl solution at 5 °C. The column gave five bands. The last eluate was found to be $[Cr(mal)_3]^{3-}$ by absorption spectra. The first, second and third eluates were found to contain two molecules of pyridine per Cr^{3+} ion by chromium ion analyses

*Author to whom correspondence should be addressed.
**Present address: Auburn University, Auburn, AL, USA.

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and the absorption intensity (the molar absorbance $\epsilon = c.5300$) of the coordinated pyridine intraligand π–π^* transition at 259 nm. The first eluate was identified as the same complex with the one obtained by the previous precipitation method. Each of the QAE-Sephadex anion exchangers on which the second and third bands were adsorbed were removed from the column and washed successively with water and methanol. Each band was reloaded on a separate QAE-Sephadex C-25 column in methanol. Each column was eluted with 0.05 M LiCl methanol solution at 5 °C. Each major band was found to be the desired complex from the absorption spectra. Each eluate was evaporated by a rotary evaporator with a dry-ice-cooled condenser *in vacuo* near 0 °C. To the condensed solution of the second eluate was added a large amount of acetone. A red powder was obtained. This was recrystallized from water and acetone. Since the third band complex could not be precipitated with acetone, it was necessary to add ether in addition to acetone to the condensed solution of the eluate. During the recrystallization, the third band seemed to be decomposed because it was found that the absorption spectra for each fractional precipitation with methanol–ether changed. The later fractions which showed the absorption band maximum at 536 nm were collected. The purity of this complex was monitored by QAE-Sephadex column chromatography. The absorption data for the first band are: λ_{max} (nm) (ϵ) 538 (30.8); 382 (26.8). The second and the third bands are denoted as the *cis*-I and *cis*-II isomer, respectively.

Preparation of ethylenediamine, N,N-dimethylethylenediamine and 2-aminomethylpyridine (amp) complexes

These complexes were prepared by a manner similar to that for the corresponding ethylenediamine complex [4]. The first and second eluates from QAE-Sephadex column chromatography with use of 0.05 M sodium chloride solution for each complex were collected and condensed to dryness. These were purified by extracting with methanol several times to remove sodium chloride. The first and the second eluates are denoted as the *cis*-I and *cis*-II isomer, respectively.

Preparation of glycinato complexes

A mixture of 3.7 g of *cis*-$K[Cr(mal)_2(H_2O)_2]\cdot 3H_2O$ (0.01 mol) and 2.5 g of glycine (0.033 mol) was dissolved in 10 cm^3 of water at 30 °C. To this solution was added 0.7 g of potassium carbonate slowly with stirring. After this mixture was allowed to stand for a few hours at room temperature, the color of the solution changed from dark violet to violet. This was diluted with 4 dm^3 of cold water and loaded on a column (4.5×55 cm) of QAE-Sephadex anion exchanger in the chloride form. It was eluted with 0.05 M NaCl solution. The column gave five bands. Each eluate of the third and fourth bands was reloaded on a separate QAE-Sephadex column after diluting it with a ten-fold volume of cold water. Each column was washed with 0.01 M $CaBr_2$ solution and then eluted with 0.5 M $CaBr_2$ solution at 5 °C. To each eluate was added a large amount of cold acetone, and the mixture was stored in a freezer. Each red precipitate was recrystallized from a small amount of water and methanol. The third and fourth eluates are described as the *cis*-I and *cis*-II isomer, respectively.

Preparation of oxalato complexes

A mixture of 3.7 g of *cis*-$Na[Cr(mal)_2(H_2O)_2]\cdot 3H_2O$ (0.01 mol) and 1.84 g of $K_2C_2O_4\cdot H_2O$ (0.01 mol) in 20 cm^3 of H_2O was heated at 50 °C for 5 h. The color of the solution changed from red–violet to greenish blue–violet. The resultant solution was poured onto a column (6×55 cm) of QAE-Sephadex C-25 (Cl^- form) anion exchanger. After washing the column with water, it was eluted with 0.15–0.23 M NaCl solution. The column gave three bands. The first eluate was found to be the starting complex (*cis*-$[Cr(mal)_2(H_2O)_2]^-$) by measuring the absorption spectra. After the second and third eluates were condensed to a small amount, the complex was extracted with methanol. The contaminating sodium chloride was removed by filtration. This procedure was repeated a few times. Finally, to the solution was added an appropriate amount of barium perchlorate in methanol. Then, each green precipitate was obtained. Each barium salt was converted to its potassium salt by metathesis with potassium sulfate. The second and third eluates are denoted as the *cis*-I and *cis*-II isomer, respectively.

Preparation of acetylacetonato complexes

A solution of *cis*-$K[Cr(mal)_2(H_2O)_2]\cdot 3H_2O$ (1.4 g) in 8 cm^3 of water was mixed with an aqueous solution (6 cm^3) of acetylacetone (0.8 g) and KOH (0.42 g). The solution was warmed at 30 °C for 4 h with stirring. Red crystals of $[Cr(acac)_3]$ were deposited. These were collected by filtration. The blue–violet filtrate was poured onto a QAE-Sephadex column (3×90 cm). The charged complex was eluted with aqueous 0.01 M NaCl solution. One violet band (band I) was eluated. After collecting this eluate, the column was eluted with 0.08 M NaCl solution and gave two bands (bands II and III). Each eluate was concentrated to dryness and extracted with methanol. This procedure was repeated several times to remove NaCl. Each precipitate was recrystallized from water and acetone. From chromatographic behavior and elemental analyses, band I was found to be $Na[Cr(mal)(acac)_2]$, and bands II and III were isomers of $Na_2[Cr(mal)_2(acac)]$. Bands II and III are denoted as the *cis*-I and *cis*-II isomer, respectively.

Deuteration of the complexes and ligands

The deuteration of the malonato methylene was performed by the following method. After dissolving the protic complexes in weakly basic D_2O solutions for several hours, they were isolated by adding acetone. The deuterated acetylacetone was prepared by the method of Egan *et al.* [5]. The deuteration of glycine was carried out by the method of Gillard *et al.* [6]. Deuterated pyridine (py-d_5) was purchased from Aldrich Chemicals.

Determination of the charge of the complexes

The charge of the pyridine complexes was determined by means of ion-exchange resin (Dowex 1×8 (Cl^--form; 200–400 mesh)) according to the method of Cady and Connick [7]. The concentration of chromium complexes was determined by the spectrophotometric method for the oxidized solution in alkaline hydrogen peroxide with use of the molar absorptivity of the chromate(VI) ion ($\epsilon = 4830$ mol^{-1} dm^3 cm^{-1}) at 372 nm.

Physical measurements

The absorption spectra were recorded by a Shimadzu UV-240 spectrophotometer in aqueous solution at room temperature. The ^2H NMR spectra of the deuterated malonato and acetylacetonato complexes were measured in 1 mM $HClO_4$ and H_2O, respectively, at ambient temperature under conditions previously described in detail [8] by a Nicolet NT-200 at Washington State University and/or a Jeol 270 GX spectrometer at Nara Women's University.

Results and discussion

Characterization of the bis(malonato) complexes

From elemental analysis (Table 1) of the bis(pyridine) complex, three eluates (B I, B II, and B III) from the column chromatography of the preparative solution are isomers having the chemical composition of $[Cr(mal)_2(py)_2]^-$. The first eluate was assigned a *trans* configuration in view of the chromatographic behavior and the lower molar absorptivity for the ligand field bands as well as the fact that only one NMR signal of malonato deuterons is observed. The other two isomers give very similar ligand field absorption spectra and two ^2H NMR signals. Thus they are *cis*-$[Cr(mal)_2(N)_2]$ type complexes. No shift of the absorption spectra at pH 10 to the longer wavelength indicates that these complexes contain the coordinated bidentate malonate ligand. In addition, the charge of both complexes is found to be -1 by the method of ion-exchange resin in agreement with the column chromatographic behavior. This fact eliminates the possibility of a binuclear structure such as $[Cr_2(\mu\text{-}mal)_2(mal)_2(py)_4]^{2-}$.

The faster eluate (*cis*-I) is a normal *cis* isomer, whereas the later one (*cis*-II) seems to be a new *cis* isomer in view of the lower stability and smaller yield than the former complex, the formation ratio of the *cis*-I isomer to the *cis*-II isomer being about 5:1 for the pyridine complexes. A similar situation is encountered with other bis(malonato) complexes, e.g. $[Cr(mal)_2(L)_2]$ ($(L)_2$ = en, *N*,*N*-Me_2-en, amp, acac, ox, or gly) as described in 'Experimental', i.e. the elemental analyses (Table 1) and column chromatography indicate that the *cis*-I and *cis*-II isomers have the chemical composition of $[Cr(mal)_2(L)_2]^{n-}$. The intensity ratio of the first to the second ligand field absorption band of the *cis*-II isomers differs meaningfully by more than 10% from that of the *cis*-I isomers; $\epsilon_{1st}/\epsilon_{2nd}$ is always *c.* 0.95 for the *cis*-II complexes and *c.* 1.10 for the *cis*-I isomer and the ratios for these values of *cis*-I and *cis*-II isomers, $(\epsilon_{1st}/\epsilon_{2nd})_I/(\epsilon_{1st}/\epsilon_{2nd})_{II}$, are 1.12–1.20 (see Table 2).

These two *cis* isomers also show characteristic differences in their stability and chromatographic behavior.

TABLE 1. Elemental analytical data of the complexes

		Found (calc.) (%)		
		C	H	N
trans-$Na[Cr(mal)_2(py)_2]\cdot 2H_2O$		49.50(40.60)	3.90(3.83)	6.16(5.92)
cis-$Li[Cr(mal)_2(py)_2]\cdot 3.5H_2O$	(I)	38.59(39.60)	4.17(4.37)	5.54(5.78)
cis-$Li[Cr(mal)_2(py)_2]\cdot 0.5H_2O\cdot 0.5CH_3OH\cdot 1.5LiCl$	(II)	38.87(38.77)	3.46(3.36)	5.49(5.49)
$Na[Cr(mal)_2(N,N\text{-}Me_2\text{-}en)]\cdot 2.5H_2O$	(I)	30.27(29.13)	5.26(5.13)	7.04(6.79)
$Na[Cr(mal)_2(amp)]\cdot 2.25H_2O$	(I)	33.51(33.69)	3.98(3.89)	6.67(6.55)
$Ca[Cr(mal)_2(gly)]\cdot 0.15CaBr_2\cdot 0.5CH_3OH\cdot 4H_2O$	(I)	21.52(21.62)	3.88(3.84)	2.87(2.97)
$Ca[Cr(mal)_2(gly)]\cdot 0.17CaBr_2\cdot 6H_2O$	(II)	18.73(18.76)	3.90(3.93)	2.73(2.73)
$K_3[Cr(mal)_2(ox)]\cdot 3H_2O$	(I)	18.78(18.64)	1.89(1.96)	
$K_3[Cr(mal)_2(ox)]\cdot K_2SO_4\cdot 3H_2O$	(II)	13.86(13.93)	1.46(1.48)	
$Na_2[Cr(mal)_2(acac)]\cdot 2.5H_2O$	(I)	30.71(29.61)	3.71(3.61)	
$Na_2[Cr(mal)_2(acac)]\cdot 2.5H_2O$	(II)	29.47(29.61)	3.82(3.61)	

TABLE 2. Absorption maxima for $[Cr(mal)_2XY]$ type complexes

XY		1st band λ(nm) (ε)	2nd band λ(nm) (ε)	$(\epsilon_{1st}/\epsilon_{2nd})$	(I/II)[a]
$(py)_2$	I	539 (63.1)	400 (55.1)	1.15	
	II	536 (72.9)	399 (75.7)	0.96	1.18
en	I	532 (66.1)	397 (58.9)	1.12	
	II[b]	532 (72.4)	397 (72.4)	1.00	1.12
N,N-Me_2-en	I	541 (72.4)	400 (67.6)	1.07	
	II[b]	541 (70.8)	397 (75.9)	0.93	1.15
amp	I	535 (67.6)	405 (60.3)	1.05	
	II[b]	535 (75.9)	397 (81.3)	0.93	1.13
gly	I	553 (67.6)	405 (60.3)	1.12	
	II	550	399	0.90[c]	1.24
ox	I	572 (72.4)	419 (72.4)	1.00	
	II	569 (89.1)	419 (107.2)	0.83	1.21
acac	I	565 (64.6)	388 (131.8)[d]		
	II	565 (81.3)	388 (131.8)[d]		

[a]The ratio for the intensity ratios $(\epsilon_{1st}/\epsilon_{2nd})_I/(\epsilon_{1st}/\epsilon_{2nd})_{II}$. [b]On the basis of the determination of Cr^{3+} concentration. [c]From qualitative absorption measurement; the quantitative data could not be obtained owing to the low solubility. [d]The absorption band at 388 nm is not due to the d–d ligand field transition.

The *cis*-II isomers are usually less stable in aqueous solution and are eluted more slowly than the *cis*-I isomers. In addition, there are some differences in the ^2H NMR spectra for these *cis* isomers, i.e. the shift differences of ^2H NMR signals for the *cis*-II isomers are smaller than those for the *cis*-I isomers, whereas these isomers of the deuterated gly and acac complexes give a small but significant difference in the ^2H NMR contact shifts as shown in Table 3. For the deuterated pyridine complexes, two sets of three ^2H NMR signals are observed for the *cis*-II isomer in contrast to the observation of a single set of three signals for the *cis*-I isomer (Table 3), suggesting the existence of the rotational isomer due to two coordinated pyridines in these complexes. These differences in NMR signals may arise from a slight difference in stereochemical and/or electronic properties for the *cis* structure between these isomers but cannot necessarily account for the stereochemical isomerism due to the fixed conformations of the malonate chelate ring.

At present there is no way to determine what kind of isomerism the *cis*-II isomers exhibit, other than by X-ray single crystal analysis.

TABLE 3. ^2H NMR chemical shifts of *cis*-bis(malonato)-chromate(III) complexes

Complexes		Chemical shifts (ppm)				
$(mal\text{-}d_2)(py)_2$	(I)	56.5			−2.0	
	(II)	49.5			−4.2	
$(mal\text{-}d_2)(gly)$	(I)	52.5	38.8	23.4	4.8	
	(II)	46.2	29.9	21.2		
$(mal\text{-}d_2)_2(ox)$	(I)		29.7	20.3		
	(II)		24.5			
$(mal\text{-}d_2)_2(acac)$	(I)		35.2	21.4		
	(II)		27.0	23.8		
$(mal)(py\text{-}d_5)_2$	(I)	14.2			−26.3	−67.2
	(II)	16.5	14.5	−23.9	−26.3	−64.5
$(mal)_2(gly\text{-}d_2)$	(I)	−49.5	54.8			
	(II)	−49.8	−55.8			
$(mal)_2(acac\text{-}d_6)$	(I)	40.9				
	(II)	45.8				

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