BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1301—1304 (1969)

The Mixed Chromium(III) Complexes containing Acetylacetone and the Halogenations Thereof[*1]

Yuki Fujii,[*2] Eishin Kyuno and Ryokichi Tsuchiya

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

(Received September 9, 1968)

The following three mixed chromium(III) complexes containing acetylacetone, which had a charge of from -1 to $+1$, were prepared: $NH_4[Cr(acac)(ata)]\cdot H_2O$,[*3] $[Cr(acac)(edda)]\cdot 2H_2O$[*3] and $[Cr(acac)(edma)(H_2O)]Cl\cdot H_2O$.[*3] The halogenations at γ-position of the acetylacetonate ring were attempted in these three mixed complexes with NCS, NBS and ICl respectively in methanol and in acetic acid solutions, where NCS, NBS and ICl are abbreviated forms of *N*-chlorosuccinimide, *N*-bromosuccinimide and iodine monochloride, respectively. From an inspection of UV-spectra of the above halogenation reaction mixtures, all the three mixed complexes were confirmed to be halogenated at the γ-position of the acetylacetonate ring. Of these complexes, $NH_4[Cr(acac\text{-}Cl)(ata)]\cdot \frac{1}{2}H_2O$ and $[Cr(acac\text{-}Br)(edda)]$ were isolated as crystals from the reaction mixtures. IR-spectra measurement was also used to certify the halogen-substitution at γ-position in the above two compounds.

Electrophilic substitution reaction (S_E reaction) at γ-position of metal acetylacetonates is of interest from the view point of the chemical reaction due to the quasi-aromaticity. Based on the experimental results recently reported,[1,2] the predominant factors governing the reactivity of 1,3-dicarbonyl chelate in S_E reaction may be focussed on the following two points: (1) the electron density at the central carbon atom (γ-position) of the chelate ring (2) the degree of the steric hindrance around the central carbon of the chelate ring. Unfortunately, however, there are still very few reports that affirm the factors described above, and most researches on the reactivity of metal acetylacetonate have been focussed only on the non-electrolyte trisacetylacetonate complexes, due to easiness for treatment in organic solvents. Furthermore, there is no report that describes the reactivity of the mixed acetylacetonate complexes, except for that of the complex ion $[Co(en)_2(acac)]^{2+}$.[1,2]

In order to obtain further information on the reactivity of the mixed complexes containing acetylacetone against halogen, such complexes having different charges of -1, 0 or $+1$ were synthesized and the halogenation reaction was investigated.

Experimental

Preparation of Mixed Complexes. *1) Ammonium Acetylacetonatoammoniatriacetatochromate(III) Monohydrate,* $NH_4[Cr(acac)(ata)]\cdot H_2O$ (I).[3] Ammonium hydroxoammoniatriacetatoaquochromate(III) dihydrate, $NH_4[Cr(OH)(ata)(H_2O)]\cdot 2H_2O$ (9.9 g, 0.03 mol), was dissolved in 40 m*l* of water and heated on a water bath. Acetylacetone (3.3 g, 0.033 mol) was added to the solution with stirring and was warmed at 80—90°C for one hour. After adjusting the pH of the solution to 5—6 by adding a small amount of ammonium carbonate, it was cooled to 0°C, when purple crystals were separated out. They were recrystallized from an aqueous solution. Yield, 10.4 g (92.0%).

Found: C, 35.09; H, 4.89; N, 7.14; Cr, 13.52; H_2O, 4.69%. Calcd for $NH_4[Cr(acac)(ata)]\cdot H_2O$: C, 35.21; H, 4.80; N, 7.47; Cr, 13.86; H_2O, 4.80%.

2) Acetylacetonato-N,N'-ethylenediaminediacetatochromium(III) Dihydrate, $[Cr(acac)(edda)]\cdot 2H_2O$ (II). Ethylenediaminediacetic acid, $eddaH_2$,[4] (8.0 g) was added to a solution of chromium(III) chloride hexahydrate (5.3 g) in 40 m*l* of water. Heating it on a water bath, the pH of the solution was adjusted to about 3 or 4 with ammonium carbonate and then acetylacetone (2.0 g, 0.02 mol) was, with stirring, added to the solution. Adjusting the pH of the resultant solution to about 7, it was cooled to 0°C. Purple crystals were then separated out and recrystallized from 50% methanol-water solution. Yield, 1.6 g (22.2%).

[*1] Presented at the 17th Symposium on Coordination Compounds of The Chemical Society of Japan, Hiroshima, Dec., 1967.

[*2] Present address: Department of Chemistry, Faculty of Science, Ibaraki University, Mito.

[*3] Abbreviations used are as follows: acac=anion of acetylacetone in enol form, ata=ammoniatriacetate anion, edda=ethylenediaminediacetate anion, and edma=ethylenediaminemonoacetate anion.

1) J. P. Collman, *Adv. Chem. Ser.*, No. 37, 78 (1963).

2) J. P. Collman, *Angew. Chem.*, **77**, 154 (1965).

3) A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **40**, 2317, 2322 (1967).

4) M. Mori, M. Shibata, E. Kyuno and F. Maruyama, *ibid.*, **35**, 75 (1962).

Found: C, 36.71; H, 5.74; N, 7.62; Cr, 14.03; H_2O, 10.0%. Calcd for $[Cr(acac)(edda)]\cdot 2H_2O$: C, 36.56; H, 5.78; N, 7.75; Cr, 14.39; H_2O, 9.98%.

3) Acetylacetonatoethylenediaminemonoacetatoaquochromium(III) Chloride Monohydrate, $[Cr(acac)(edma)(H_2O)]Cl\cdot H_2O$ (III). Ethylenediaminemonoacetic acid dihydrochloride monohydrate, $edmaH\cdot 2HCl\cdot H_2O$*4 (4.2 g, 0.02 mol), was added to the solution of chromium(III) chloride hexahydrate (5.3 g, 0.02 mol) in 30 m*l* of water. Heating the solution on a water bath, the solution was adjusted to about pH 2 or 3 with ammonium carbonate. Acetylacetone (2.0 g, 0.02 mol) neutralized with equimolar ammonium carbonate was added to the solution, and was heated for an hour. After the pH of the solution was adjusted to about 5, it was allowed to stand for about three weeks at room temperature. Reddish purple crystals were separated out and recrystallized from an aqueous solution. Yield, 2.7 g (40%).

Found: C, 31.98; H, 5.85; N, 7.88; Cr, 14.61; H_2O, 5.02%. Calcd for $[Cr(acac)(edma)(H_2O)]Cl\cdot H_2O$: C, 31.81; H, 5.95; N, 8.25; Cr, 15.31; H_2O, 5.30%.

Isolation of Halogenated Mixed Complexes. *1) Ammonium 3-Chloroacetylacetonatoammoniatriacetatochromate(III) Hemihydrate,* $NH_4[Cr(acac\text{-}Cl)(ata)]\cdot \frac{1}{2}H_2O$ (IV). The solution of NCS (5.4 g, 0.04 mol) in 60 m*l* of glacial acetic acid was slowly added to the solution of the complex I (7.5 g, 0.02 mol) in glacial acetic acid at room temperature.[5] After being stirred for 30 min, 150 m*l* of ether was added and the resultant reddish purple precipitates were collected. Washed with ether, the powder obtained was dissolved in 70 m*l* of ethanol at 40°C. Fifty milliliters of ether were added to the solution and the reddish purple precipitates produced were collected. Washed with ether, the precipitates were recrystallized from 20% of methanol solution. Black purple crystals were separated out. Yield, 2.1 g (25.5%).

Found: C, 32.20; H, 4.49; N, 6.70; Cr, 12.36; Cl, 8.26; H_2O, 2.20%. Calcd for $NH_4[Cr(acac\text{-}Cl)(ata)]\cdot \frac{1}{2}H_2O$: C, 32.99; H, 4.28; N, 6.99; Cr, 12.96; Cl, 8.85; H_2O, 2.25%.

2) 3-Bromoacetylacetonatoethylenediaminediacetatochromium(III), $[Cr(acac\text{-}Br)(edda)]$ (V). One gram (0.003 mol) of the complex II was dissolved in 60 m*l* of methanol and a solution of NBS (0.6 g, 0.003 mol) in methanol was added to it at room temperature. Evaporating off the solvent at room temperature, purple crystals were separated out. These were insoluble in various solvents. Yield, 0.6 g (66.0%).

Found: C, 32.81; H, 4.13; N, 6.95; Cr, 12.88; Br, 19.26%. Calcd for $[Cr(acac\text{-}Br)(edda)]$: C, 32.68; H, 4.00; N, 6.93; Cr, 12.87; Br, 19.77%.

Apparatus. The molar conductivity, the UV and visible absorption spectra and IR spectra were measured with a Yokogawa Universal Bridge BV-Z-13A, a Hitachi EPS Spectrophotometer and a Nippon Bunko DS-301 Infrared Spectrometer, respectively. The quantity of the crystalline water contained in these compounds was estimated from TGA curves measured with Derivatograph.

Results and Discussion

Visible and UV Absorption Spectra. Absorption spectra for the complexes I, II, III and IV are shown in Fig. 1 and the numerical values of the absorption bands for these complexes, including those for the other related compounds halogenated, are summarized in Table 1.

The absorption spectrum of the complex I has a band at 330 mμ which is characteristic of the coordinated acetylacetone but the maximum of the corresponding band in complex IV is shifted to 350 mμ. The spectra measured for the reaction mixtures of the complex I and NBS and those of I and ICl in methanol and in acetic acid solutions also show the shifts of the absorption maxima to 351 mμ and 357 mμ, respectively (These compounds are presumed to have the formulae, $NH_4[Cr(acac\text{-}Br)(ata)]$ and $NH_4[Cr(acac\text{-}I)(ata)]$, respectively.). Such a red shift of the maximum mentioned above which is assigned to $d\varepsilon \rightarrow \pi_4$ transition[6] will show evidence of halogenation in

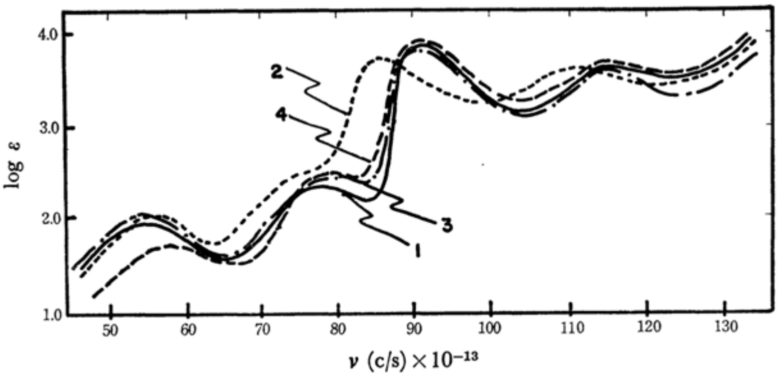

Fig. 1. The absorption spectra of the mixed complexes.
1: I (in H_2O), 2: IV (in H_2O), 3: II (in CH_3OH), 4: III (in CH_3OH)

---

*4 The preparation will be published elsewhere.

[5] J. P. Collman, R. A. Moss, H. Maltz and C. C. Heidel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

[6] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

TABLE 1. UV SPECTRA OF THE MIXED COMPLEXES

Complex	mμ ($d_\varepsilon \rightarrow \pi_4$)	($\log \varepsilon$)	Solvent
$NH_4[Cr(acac)(ata)] \cdot H_2O$ I	331	(3.85)	CH_3OH, H_2O
$NH_4[Cr(acac\text{-}Cl)(ata)] \cdot \frac{1}{2}H_2O$ IV	350	(3.79)	CH_3OH, H_2O
$NH_4[Cr(acac\text{-}Br)(ata)]$*	351		CH_3OH, CH_3COOH
$NH_4[Cr(acac\text{-}I)(ata)]$*	357		CH_3OH, CH_3COOH
$[Cr(acac)(edda)] \cdot 2H_2O$ II	330	(3.80)	CH_3OH
$[Cr(acac\text{-}Cl)(edda)]$*	350		CH_3OH
$[Cr(acac\text{-}Br)(edda)]$ V	351	(3.60)	CH_3OH, H_2O
$[Cr(acac\text{-}I)(edda)]$*	357		CH_3OH
$[Cr(acac)(edma)(H_2O)]\text{-}Cl \cdot H_2O$ III	331	(3.87)	CH_3OH
$[Cr(acac\text{-}Cl)(edma)(H_2O)]\text{-}Cl$*	350		CH_3COOH
$[Cr(acac\text{-}Br)(edam)(H_2O)]\text{-}Cl$*	351		CH_3OH
$[Cr(acac\text{-}I)(edma)(H_2O)]\text{-}Cl$*	359		CH_3OH

* Although these complexes could not be isolated, their compositions were presumed on the basis of IR spectra measurement in the respective mixed solutions.

TABLE 2. IR SPECTRA OF THE MIXED COMPLEXES (cm^{-1})

Ccomplex	ν_{O-H}	ν_{N-H}	ν_{COO-Cr}	$\nu_{C=O(acac)}$	$\nu_{C=C}$
I	3620	3060 3180 3380	1650 1670	1570	1528
IV	3520	3040 3180 3390	1650	1560	
II	3400 3500	3140 3260	1635 1675	1560	1515
V		3100 3180 3250	1670	1550	
III	3410	3080 3140 3200 3270	1640	1560	1530

the acetylacetonate ring[2] and this explanation can be ascertained by the fact that neither acetylacetone nor NCS (also NBS and ICl) has absorption peak near 355 mμ.

The maximum of the characteristic absorption band for the complex II appears at 330 mμ and the spectrum of the bromo-substituent V has a corresponding maximum at 351 mμ. The spectra of the chloro- and iodo-substituents (probably having the formulae, $[Cr(acac\text{-}Cl)(edda)]$ and $[Cr(acac\text{-}I)(edda)]$, respectively), which were measured for the reaction mixture of the complex II and NCS or ICl in methanol solution, (the reaction in acetic acid made the complex II to $[Cr(eddaH)_2]X \cdot 3H_2O$,*[4] where X is halogen anion) have the maxima at 350 mμ and 357 mμ, respectively.

The maximum of the complex III appears at 331 mμ. The spectra for the complexes, which may be considered to be expressed by $[Cr(acac\text{-}X)(edma)(H_2O)]Cl$ (X=Cl, Br and I), were measured for the reaction mixtures of the complex III and halogenating reagents in acetic acid and in methanol. The band of the complex III at 331 mμ is shifted to 350 mμ by chlorination in acetic acid, but in methanol as a solvent only a small distinct shoulder appears at 350 mμ. The band at 331 mμ is also shifted to 351 mμ by bromination and to 359 mμ by iodination in methanol solvent, but in the case of acetic acid solvent, complex III decomposed very rapidly before absorption measurement.

IR Spectra. The predominant bands of IR spectra measured in the region 4000—700 cm^{-1} are listed in Table 2. The strong bands appearing between 1650 and 1670 cm^{-1} in the complexes I and IV indicate the presence of three coordinated carboxyl groups of ata. The strong bands of 1528 and 1570 cm^{-1} in the complex I are assigned to $\nu_{C=C}$ and $\nu_{C=O}$ in the coordinated acetylacetonate, respectively. In the complex IV, however, only one peak at 1560 cm^{-1} for coordinated acetylacetonate is observed in this region. This phenomenon is well known in a number of metal acetylacetonate and is commonly used to check the presence of the γ-substituted chelate ring.[1]

The spectra of the complexes II and III indicate the strong bands between 1630 and 1680 cm^{-1} for $\nu_{\text{M-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}}$ of coordinated edda and edma respectively and also have two strong bands characteristic of coordinated acetylacetone between 1510 and 1560 cm^{-1}. On the other hand, the spectrum of the complex V indicates only one band at 1550 cm^{-1} for acetylacetone, which suggests the substitution at γ-position.

Conductivity Measurements and Behavior toward Ion-exchangers. The values of molar conductivity of the complexes prepared in this work measured in a 1/500 mol aqueous solution at 25°C and the behavior toward ion-exchangers are summarized in Table 3, in which the symbol + indicates the possibility of the adsorption of the complexes by the resin and −, the reverse. It is found from this table that the three complexes I, II and III have the charges of −1, 0 and +1 respectively and the charges are still invariable by halogenation both in I and II.

Reactivity of the Mixed Complexes against Halogenating Agents. It may be concluded from the results obtained above that the three mixed complexes I, II and III are halogenated at

Table 3. Molar conductivity and behavior toward ion exchangers

Complex	Molar conductivity (mho cm^{-1})	Ion exchanger Na-form	Cl-form
I	104.7	−	+
IV	104.2	−	+
II	—	−	−
V	—	−	−
III	102.8	+	−

γ-position of the chelate ring irrespective of the charge in the complex ions themselves from -1 to $+1$. But the complex III which has the charge $+1$ is relatively difficult to be halogenated as compared with complex I or II. This result suggests that the positively charged complex is not as easily attacked by the electrophilic reagent, which also has positive charge, as the negatively charged or non-charged complex. This result coincides with that obtained by Collman for cobalt(III) complex and indicates that the electron density at the γ-position of acetylacetonate ring in the positively charged complex is somewhat more deficient than that of negatively charged or non-charged complexes.[1,2]

Some differences in the reactivity were observed, depending upon the solvent, and the halogenation was more vigorous in acetic acid than in methanol. NCS was milder than NBS or ICl as halogenating reagent in both solvents.