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Preparations and Paramagnetic Contact Shifts of Some Tris(β-diketonato)vanadium(III) Complexes

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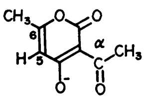
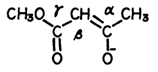
Synopsis. New tris(dehydroacetato)-, tris(methyl acetoacetato)-, and tris(ethyl acetopyruvato)vanadium(III) complexes were prepared and characterized by IR and NMR spectroscopies. Paramagnetic contact shifts of these complexes were discussed.

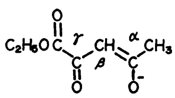
Remarkable paramagnetic contact shifts have been observed for mononuclear trivalent vanadium complexes containing univalent chelate ligands such as β-diketonato,1–3) salicylaldehydato,4) and their related ligands,4,5) and been applied to the investigations of the *fac-mer* stereochemistry and of electron distributions over the ligands of these complexes.2,3,6,7) However, no work has been yet reported about a vanadium(III) complex coordinated with dehydroacetic acid (Hdac), alkyl acetoacetate, or alkyl acetopyruvate, each of which belongs to a β-diketone, possessing a characteristic substituent. This note will deal with the preparation and ^{1}H-NMR study of the new vanadium(III) complexes containing dac, methyl acetoacetato (maa), or ethyl acetopyruvato (eap) ligand.



dac



maa



eap

Experimental

Materials. Commercial grade vanadium(III) chloride, dehydroacetic acid, and methyl acetoacetate were used without further purification. Ethyl acetopyruvate was prepared acconding to the method of Marvel *et al.*8)

General Procedures. IR and ^{1}H-NMR spectra were measured on a Hitachi Model 285 and a JEOL Model PS-100 (100 MHz) spectrometers, respectively. Since solutions of vanadium(III) complexes appeared to be sensitive to aerial oxidation, preparations and recrystallization were carried out under a dinitrogen atmosphere.

Preparation of [*V(dac)*$_3$]. An aqueous solution of dehydroacetic acid (57 mmol) and sodium carbonate (30 mmol) was added to an aqueous solution of vanadium(III) chloride (19 mmol). After the mixture was refluxed for 2 h, a resulting precipitate was separated, washed with water, and dried *in vacuo*. Recrystallization from dichloromethane–petroleum ether yielded an ochre-colored solid, [V(dac)$_3$].

Preparation of [*V(maa)*$_3$]. An ethanol solution of methyl acetoacetate (19.2 mmol) and an aqueous solution of sodium carbonate were added to vanadium(III) chloride (6.4 mmol) in 32 cm^3 of an ethanol–water (3: 1) solution. The mixture was stirred for 2 h at room temperature. After the solvent was evaporated, a residue was recrystallized from benzene–petroleum ether to give a greenish yellow crystal, [V(maa)$_3$].

Preparation of [*V(eap)*$_3$]. Sodium ethyl acetopyruvate (30 mmol) was added to an aqueous solution of vanadium(III) chloride (9 mmol). After the reaction mixture was refluxed for 1 h, a resultant precipitate was separated, washed with water, and dried *in vacuo*. Recrystallization from diethyl ether–petroleum ether afforded a reddish brown solid, [V(eap)$_3$]. This complex is considerably sensitive to air.

Results and Discussion

Table 1 shows the yields, elemental analyses, and some properties of the complexes prepared in the present study. IR spectrum of [V(maa)$_3$] lacked ν(C=O) near 1700 cm^{-1}, revealing that the vanadium(III) ion was coordinated with a carbonyl oxygen of the ester group to form a β-diketonato chelate ring, but not with a methoxy oxygen of the same group. Moreover, IR spectra of the three complexes exhibited complicated bands near 1510 and 1590 cm^{-1}, which were assignable to the unsymmetrical β-diketonato chelate rings. The reasons for the complicacy of these bands were probably due to the coexistence of two kinds of bonding sites in the unsymmetrical β-diketonato ligand itself, the *fac-mer* isomerism, and the coordination of the three chelate rings in different circumstances in the *mer* isomer, as elucidated by ^{1}H-NMR spectra.

Table 2 shows ^{1}H-magnetic resonances of [V(dac)$_3$], [V(maa)$_3$], and [V(eap)$_3$]. Four signals were detected for a given substituent on the unsymmetrical chelate ring of each of these complexes. This fact indicates that these complexes consist of *fac* and *mer* isomers, similarly to the other vanadium(III) complexes with unsymmetrical β-diketonato ligands.2,3) Three signals of an equal intensity were ascribed to the substituents on the three

TABLE 1. YIELDS AND PROPERTIES OF THE VANADIUM COMPLEXES

Complex	Yield (%)	Mp$^{a)}$ (°C)	Characteristic IR bands (cm^{-1})$^{b)}$		C(%)		H(%)	
			β-Diketonato ring$^{c)}$	Other ν(C=O)	Calcd	Found	Calcd	Found
[V(dac)$_3$]	78	147—150	1552, 1565	1720$^{d)}$	52.19	51.96	3.83	4.31
[V(maa)$_3$]	41	152—154	1510, 1590	—	45.47	45.62	5.34	5.36
[V(eap)$_3$]	10	63	1508, 1582	1727, 1740$^{e)}$	48.29	48.03	5.21	4.98

a) In dinitrogen atmosphere. b) In KBr disc. c) A few shoulders were observed near each band. d) Pyrone carbonyl. e) Ester carbonyl.

Table 2. ^{1}H-NMR data of the vanadium complexes[a)]

Complex	Isomer ratio[b)] (%)		α-CH_3 δ, ppm	β-H δ, ppm	γ-Substituents	
					δ, ppm	δ, ppm
[V(dac)$_3$]	*fac*	18	50.4	—	0.8[c)]	22.1[d)]
	mer	82	54.9, 61.5, 63.5	—	1.2, 11.1, 11.6[c)]	17.2, 19.6, 22.4[d)]
[V(maa)$_3$]	*fac*	12	25.8	31.8	9.5[e)]	—
	mer	88	17.3, 21.5, 27.5	41.0, 41.5, 55.2	9.0, 10.7, 12.4[e)]	—
[V(eap)$_3$]	*fac*	17	60.2	39.9	6.0, 6.3[f,h)]	1.1[g,h)]
	mer	83	57.6, 64.0, 69.2	26.5, 45.8, 56.0		

a) Measured at 20 °C in deoxygenated $CDCl_3$ using tetramethylsilane as the internal standard. b) Calculated from α-CH_3 signals. c) 5-H. d) 6-CH_3. e) OCH_3. f) $COOCH_2$–. g) –CH_3(Et). h) Not distinguished owing to overlapping each other.

unsymmetrical chelate rings in the disparate circumstances in the *mer* isomer. The fourth signal was ascribed to that on the three unsymmetrical chelate rings in the same circumstance, *i.e.* in C_3 symmetry in the *fac* isomer. Since the fourth signal is smaller than each of the former three ones, the *fac* isomer populates in a smaller ratio than that expected for a statistical formation, which would result in a *fac*: *mer* ratio of 1: 3 and in four signals of an equal intensity for the ring substituents.

Holm *et al.*[2)] reported that in the NMR paramagnetic shifts of tris(β-diketonato)vanadium(III) complexes, π-contact part was dominant and pseudo-contact one was negligible, and that unpaired spin of the metal was delocalized to the β-diketonato ligand. In connection with the Holm *et al.*'s explanations, the paramagnetic shifts of α-CH_3 protons of [V(maa)$_3$], [V(eap)$_3$], and the related (β-diketonato)vanadium(III) complexes[1–3)] were correlated to the electronic effect of the corresponding γ-substituent of the β-diketonato ligand. A value σ_R^m [9)] was used as a parameter for the electronic effect of the γ-substituent, since the β-diketonato conjugated system was reported to have a quasi-aromatic character[10)] and σ_R^m represents the term of the resonance effect of each *meta* substituent, composing Hammett value σ^m.[9)]

Figure 1 presents the paramagnetic shifts of the α-CH_3 protons[11)] against the σ_R^m values of the γ-substituents. As for [V(maa)$_3$], α-CH_3 protons show a small shift, indicating that the methoxy group at the γ-position of the chelate ring suppresses the electron delocalization from the metal to the ligand. This is consistent with a negative σ_R^m value of the methoxy group, representing the donation of the resonance electron from this group. However, as for [V(eap)$_3$] in which the ethoxycarbonyl group has a positive σ_R^m, meaning the small donating ability of the resonance electron, the contact shift of α-CH_3 protons is large. The linearity shown in Fig. 1 is consistent with the quasi-aromatic character of the β-diketonato systems, and supports the Holm *et al.*'s explanations[2)] about the paramagnetic shifts of the tris(β-diketonato)vanadium(III) complexes.

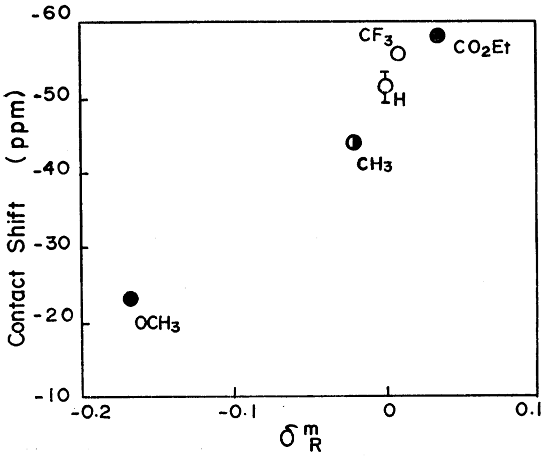


Fig. 1. Relationship between the paramagnetic shift of the α-protons and the σ_R^m value of the γ-substituent.
◑: From Ref. 1, ○: from Ref. 2, ●: from the present study. See note 11 concerning the paramagnetic shifts.

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11) The paramagnetic shifts of the α-CH_3 protons were determined from a difference between δ-value of the complex and that of the corresponding free ligand. The δ-values for the *fac*-type complexes were used as for the γ-substituents of OCH_3, CF_3, and CO_2Et. As regards the γ-substituents of CH_3 and H, δ-value of the acetylacetonato complex and the range of four δ-values for the *fac* and *mer* isomers were adopted, respectively.