Reactions of Tris(acetylacetonato)manganese(III) and Bis(acetylacetonato)manganese(II) with Ethylenediamine and Other Primary Amines

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Tris(acetylacetonato)manganese(III) reacts with ethylenediamine (L_2) and other primary amines (L) in organic solvents at room temperature producing $Mn(acac)_2L_2$. The same Mn(II) complexes were also prepared quantitatively by reactions of $Mn(acac)_2(H_2O)_2$ with amines. Besides the usual hexa-coordinate monomeric complex, allylamine gave a dimeric compound $[Mn(acac)_2(CH_2{=}CHCH_2NH_2)]_2$, which is the first example of the binuclear manganese(II) complex of acetylacetone. The stoichiometry of the redox reaction between $Mn(acac)_3$ and ethylenediamine was established and discussed in connection with the initiation mechanism of vinyl polymerization.

In previous papers, reactions of acetylacetone chelates of copper(II),[1] beryllium,[2] and aluminum[3] with bromine in dichloromethane have been reported to result in different kind of products. Similar reactions of the corresponding cobalt(III),[4] cobalt(II),[5] nickel(II),[6] manganese(III), and manganese(II) complexes are now under investigation. In the course of these studies it was noticed that primary alkylamines react with tris(acetylacetonato)manganese(III) producing amine adducts of bis(acetylacetonato)manganese(II). The same compounds have also been derived from the latter manganese(II) chelate by direct reactions with the corresponding amines.

Dwyer and Sargeson[7] synthesized bis(acetylacetonato)diamminemanganese(II) and similar adducts of 2,2′-bipyridine and 1,10-phenanthroline either by substitution reactions between bases and sodium tris(acetylacetonato)manganate(II), or by direct addition reactions between bases and bis(acetylacetonato)manganese(II). Graddon and Mockler[8] also prepared mono- and bis-adducts of pyridine derivatives with the manganese(II) chelate by reactions of bis(acetylacetonato)diaquomanganese(II) with the heterocyclic bases. However, corresponding alkyl amine adducts have not been reported as yet.[9]

As to the redox reactions, tris(acetylacetonato)manganese(III) has been reduced by phenylhydrazine[10] and 2,6-xylenol[11] but has not been reduced by biguanide,[12] picolinic acid or 8-hydroxyquinoline.[13] The present paper reports on the redox reactions between tris(acetylacetonato)manganese(III) and several aliphatic amines, and also on the characterization of manganese(II) complexes produced.

Experimental

Materials. Tris(acetylacetonato)manganese(III),[14] bis(acetylacetonato)manganese(II)[15] and bis(acetylacetonato)-diaquomanganese(II)[15] were synthesized by the methods of Charles (Found for $Mn(C_5H_7O_2)_3$: Mn, 15.59; C, 51.15; H, 5.98%. Found for $Mn(C_5H_7O_2)_2$: Mn, 21.85; C, 47.21; H, 5.58%. Found for $Mn(C_5H_7O_2)(H_2O)_2$: Mn, 19.09; C, 41.68; H, 6.29%). Bis(acetylacetone)ethylenediimine was also prepared according to the literature[16] and recrystallized twice from water (Found: C, 64.39; H, 9.02; N, 12.54%).

Methallylamine was prepared by ammonolysis of methallyl chloride.[17] In an autoclave 96 *ml* of methallyl chloride (1 mol), 500 g of 28% aqueous ammonia (8 mol) and 140 g of ammonium chloride (2.5 mol) were allowed to react at 80—90°C for about 30 min under a pressure of 10 kg/cm^2. Then an aqueous solution of 160 g of sodium hydroxide was added to the mixture and methallylamine was extracted with ether and purified by fractional distillation. Found: C, 66.41; H, 12.63%. *trans*-Crotylamine was also synthesized according to the similar method. Found: C, 67.07; H, 12.81%.

Commercial ethylenediamine, propylamine and allylamine were distilled over metallic sodium. Allylamine was allowed in advance to stand over potassium hydroxide for one day in the cold. Diethyl ether was dried with calcium chloride and distilled over sodium. Benzene and *N,N*-dimethylformamide (DMF) were also purified by the standard methods.[18]

Redox reactions. The reaction between ethylenediamine and tris(acetylacetonato)manganese(III) was performed in a

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three-necked flask equipped with a burette and a glass tube containing calcium chloride. To an ethereal solution of the manganese(III) complex (*ca.* 0.3 g) was added dropwise an ethereal solution of three times as many moles of ethylenediamine with magnetic stirring. Agitation was continued further after mixing of reactant solutions was finished. After about half an hour a precipitate of ivory color began to separate, but it took about one week before intense black-brown color of the starting solution disappeared indicating completion of the reaction. Then the precipitate was filtered and submitted to the elemental analysis. The filtrate was divided into three portions and contents of acetylacetone, ethylenediamine and total nitrogen were determined.

Analyses. Manganese content in each solid sample was determined gravimetrically as the sulfate after decomposition of the compound with nitric acid.

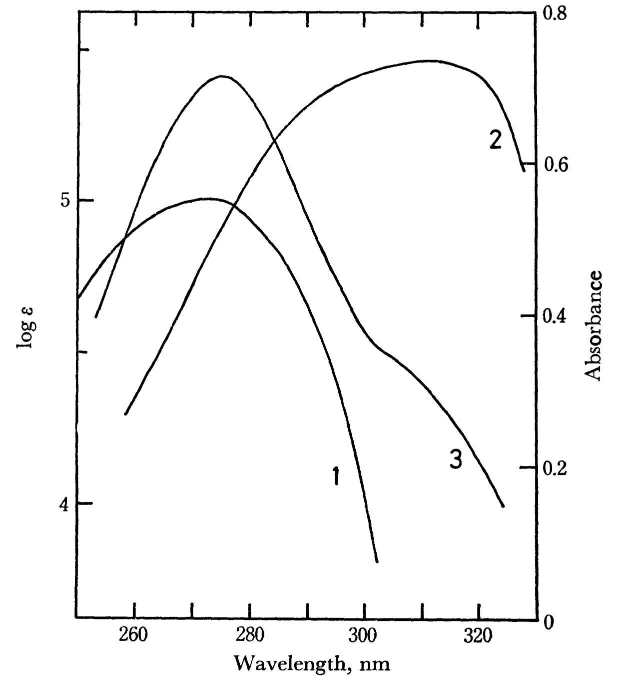

Fig. 1. Ultraviolet absorption spectra of acetylacetone (curve 1, left ordinate), bis(acetylacetone)ethylenediimine (curve 2, left ordinate), and a filtrate from the redox reaction between tris(acetylacetonato)manganese(III) and ethylenediamine (curve 3, right ordinate) in ether.

The filtrate from the above redox reaction contained the liberated acetylacetone, the excess ethylenediamine, produced bis(acetylacetone)ethylenediimine, and the decomposition products of ethylenediamine. The ultraviolet absorption spectrum of this solution is shown in Fig. 1 together with those of acetylacetone and bis(acetylacetone)ethylenediimine. Ethylenediamine does not absorb light in this region and its decomposition products may not either. Thus the absorption spectrum of the solution was analysed on the assumption that it is due to acetylacetone and bis(acetylacetone)ethylenediimine, and the total amount of acetylacetone freed in this redox reaction was determined.

Another aliquot of the filtrate solution was acidified with dilute sulfuric acid and freed of solvent under reduced pressure. The residue was dissolved in water and neutralized with a dilute solution of sodium hydroxide. An aqueous solution of sodium rhodizonate was added in excess to this solution producing a violet precipitate of one to one salt of ethylenediamine with rhodizonic acid. The gravimetric determination of ethylenediamine by this method was tested in advance employing a known amount of the amine, and the accuracy was proved to be more than 99%.

The third aliquot of the filtrate solution was placed in a 500 m*l* Kjeldahl flask, to which potassium sulfate (10 g), selenium (0.2 g) and concentrated sulfuric acid (25—30 m*l*) were added. The mixture was carefully heated by an infrared irradiation to vaporize ether almost completely, and then the total nitrogen content was measured according to the usual Kjeldahl method.

Syntheses of Mixed Complexes of Manganese(II). To prevent oxidation of manganese(II) the following preparations were all performed in an atmosphere of nitrogen employing deoxygenated solvents.

Bis(acetylacetonato)ethylenediaminemanganese(II): Two methods were employed. (i) About 3 g of tris(acetylacetonato)manganese(III) was dissolved in DMF, to which a DMF solution of three times as many moles of ethylenediamine was added. After about 30 min an ivory precipitate began to separate, which was recrystallized from DMF resulting in pale yellow crystals: mp around 150°C (dec). Found: Mn, 17.55; C, 45.83; H, 7.08; N, 8.63%. Calcd for $\mathrm{Mn(acac)_2en = C_{12}H_{22}O_4N_2Mn}$: Mn, 17.54; C, 46.00; H, 7.09; N, 8.94%.

(ii) Bis(acetylacetonato)diaquomanganese(II) was allowed to react with an equimolar amount of ethylenediamine in DMF. A pale yellow precipitate appeared at once in an almost quantitative yield, and was recrystallized from DMF. Found: M, 17.51; C, 46.10; H, 7.14; N, 9.15%.

Thus, the same compound was obtained in these two types of reactions as evidenced by results of the elemental anaysis and infrared spectra. The corresponding complex containing deuterated ethylenediamine was prepared by the following method. Ethylenediamine-d_4 was prepared by repeated fractional distillations from heavy water solutions and characterized by means of NMR spectra. To a solution of 0.3 g of anhydrous bis(acetylacetonato)manganese(II) in 10 m*l* of DMF containing a few drops of heavy water was added ten drops of ethylenediamine-d_4 and allowed to react for a while with frequent shaking. Bis(acetylacetonato)(ethylenediamine-d_4)manganese(II) was produced as a pale yellow precipitate, filtered and washed with DMF containing a small quantity of heavy water.

Bis(acetylacetonato)bis(allylamine)manganese(II): This compound was also prepared by the following two methods. (i) About 2 g of tris(acetylacetonato)manganese(III) was dissolved in 200 m*l* of ether, to which more than ten times as many moles of allylamine was added. A precipitate began to appear after a while, but the mixture was stirred for one or two days. Pale yellow needles were obtained after recrystallization from ether. Found: Mn, 15.11; C, 52.16; H, 7.57; N, 7.98%. Calcd for $\mathrm{Mn(acac)_2(CH_2{=}CHCH_2NH_2)_2 = C_{16}H_{28}O_4N_2Mn}$: Mn, 14.96: C, 52.31; H, 7.68; N, 7.63%. If about six times as many moles of allylamine is employed, a mixture of bis- and mono-adducts of allylamine with bis(acetylacetonato)manganese(II) is obtained.

(ii) An ethereal solution of twice as many moles of allylamine was added to a suspension of bis(acetylacetonato)diaquomanganese(II) (3 g) in ether. Immediately appeared a pale yellow fuzzy precipitate, which was recrystallized from ether. Found: C, 52.12; H, 7.63; N, 7.30%. Infrared spectra of this specimen were identical with those of the product from the above redox reaction.

Bis(acetylacetonato)allylaminemanganese(II): When an ethereal solution of equimolar allylamine was added to an ethereal suspension of bis(acetylacetonato)diaquomanganese(II) (2.5 g), a fuzzy precipitate appeared at first, but changed gradually to a powder. Pale yellow crystals were obtained by recrystallization from ether. Found: C, 50.25; H, 6.86; N, 4.10%. Calcd for $Mn(acac)_2(CH_2{=}CHCH_2NH_2)$ = $C_{13}H_{21}O_4NMn$: C, 50.33; H, 6.82; N, 4.51%.

Bis(acetylacetonato)bis(propylamine)manganese(II): The reaction between tris(acetylacetonato)manganese(III) and propylamine in ether gave pale yellow needles. Found: Mn, 15.09; C, 51.64; H, 8.62; N, 7.45%. Calcd for $Mn(acac)_2(C_3H_7NH_2)_2{=}C_{16}H_{32}O_4N_2Mn$: Mn, 14.79; C, 51.75; H, 8.69; N, 7.54%. The same complex was also produced by the reaction of propylamine with bis(acetylacetonato)-diaquomanganese(II) in ether. Found: Mn, 14.97; C, 51.71; H, 8.63; N, 7.50%. Even when an equimolar amount of propylamine was allowed to react with the manganese(II) complex, the one to one adduct was not produced but the bis(amine)-adduct was obtained exclusively.

Bis(acetylacetonato)bis(methallylamine)manganese(II) was prepared by the reaction of bis(acetylacetonato)diaquomanganese(II) with methallylamine in ether in the mole ratio of one to two and recrystallized from ether. Found: Mn, 13.91; C, 54.55; H, 8.23; N, 7.25%. Calcd for $Mn(acac)_2(CH_2{=}C(CH_3)CH_2NH_2)_2$ = $C_{18}H_{32}O_4N_2Mn$: Mn, 13.89; C, 54.68; H, 8.16; N, 7.08%.

*Bis(acetylacetonato)bis(*trans*-crotylamine)manganese(II)* was also prepared in a similar reaction. Found: Mn, 13.71; C, 54.80; H, 8.20, N, 7.07%. Either of these allylic amines did not give the mono(amine)-adduct even in reactions at the reactants mole ratio of one to one.

Measurements. Ultraviolet absorption spectra were measured by means of a Hitachi spectrophotometer model EPS-2. Infrared absorption spectra in the 4000—650 cm^{-1} region were measured with a Hitachi infrared spectrophotometer EPI-2, and those in 700—200 cm^{-1} with a Hitachi grating infrared spectrophotometer EPI-L. Magnetic susceptibilities were measured at room temperature by the Gouy method with a Shimadzu magnetic balance employing hexaamminechromium(III) chloride as a reference substance. Diamagnetic corrections were calculated from Pascal's constants. Thermogravimetric analysis was performed using a thermo-spring-balance C-282 of Hamada Denki Seisakusho, Ltd. under reduced pressure. The rate of temperature elevation was fixed at 30°C/hr for the ethylenediamine complex and at 20°C/hr for allylamine and propylamine complexes. Molecular weight was determined by the cryoscopic method in benzene in a deaerated vessel to prevent oxidation of the manganese(II) complexes and also with a vapor-pressure osmometer of Toa electronics, Ltd. employing ether as a solvent and tris(acetylacetonato)aluminum as a reference substance.

TABLE 1. CHARACTERISTIC INFRARED BANDS OF THE DIAMINE GROUP IN BIS(ACETYLACETONATO)ETHYLENEDIAMINE-MANGANESE(II) AND THE CORRESPONDING ETHYLENEDIAMINE-d_4 COMPLEX

$Mn(acac)_2en$	$Mn(acac)_2$ (en-d_4)	ν_{NH2}/ν_{ND2}	Assignment
3278 m	2422 w	1.35	NH_2 stretch
3195 m	2340 w	1.36	
~1600[a]	1187 w	1.35	NH_2 scissor
1317 m	1000 m	1.32	NH_2 wag
1120 m	868 m	1.29	
1096 sh	860 sh	1.28	NH_2 twist
1014 s			
762 m	580	1.31	NH_2 rock

a) This band is obscured by the intense absorption of the acetylacetonate ligand.

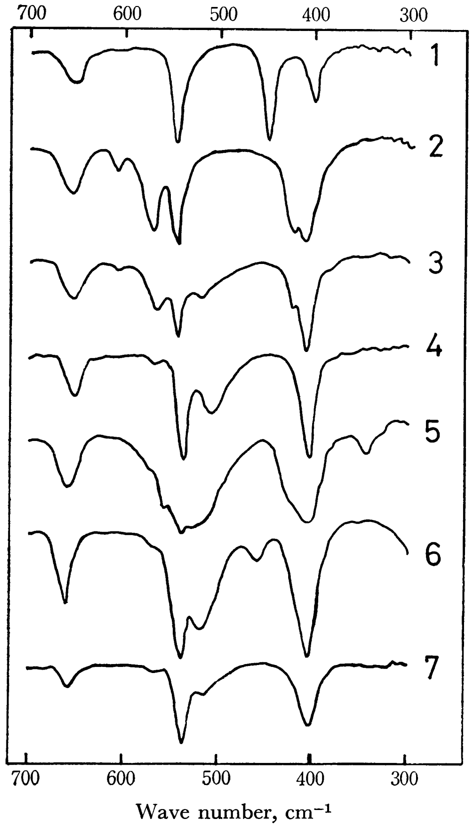

Fig. 2. Infrared spectra in the 700—300 cm^{-1} region of bis(acetylacetonato)manganese(II) and amine adducts in Nujol mull: 1, $Mn(acac)_2$; 2, mono(allylamine)-adduct; 3, bis(allylamine)-adduct; 4, bis(propylamine)-adduct; 5, bis(methallylamine)-adduct; 6, bis (*trans*-crotylamine)-adduct; 7, ethylenediamine-adduct.

Results

Properties of Bis(acetylacetonato)ethylenediaminemanganese(II). A novel mixed ligand complex bis(acetylacetonato)ethylenediaminemanganese(II) was prepared either by a redox reaction between tris(acetylacetonato)manganese(III) and ethylenediamine, or by a substitution reaction of bis(acetylacetonato)diaquomanganese(II) with the amine. Infrared absorption spectra of the compound in the higher frequency region are composed of those due to the acetylacetonate ligand and also those due to coordinated ethylenediamine. Characteristic bands due to the diamine ligand are listed in Table 1 which were assigned by reference to literatures[19] and also to the deuteration effects. As shown in Fig. 2, infrared absorption spectrum of bis(acetylacetonato)manganese(II) in the 700—300 cm^{-1} region consists of a broad band around 650 cm^{-1} and three strong peaks at 543, 449, and 399 cm^{-1}. Dismukes, Jones, and Bailar interpreted the spectrum in terms of coupling of metal-oxygen vibrational modes with three low-frequency vibrational modes of the acetylacetonate anion.[20] The strong peak at 449 cm^{-1} was not ob-

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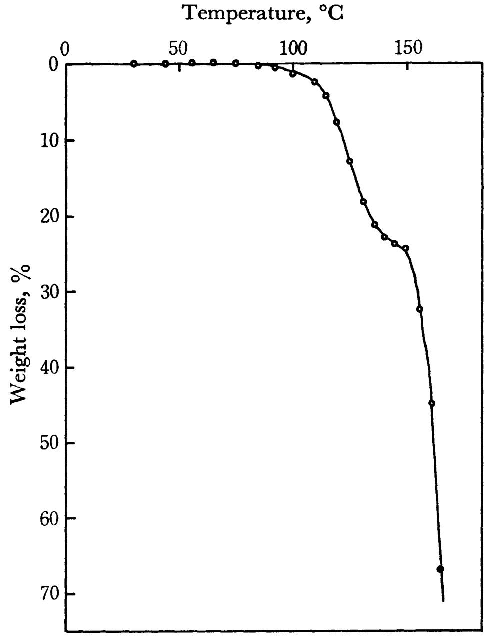

Fig. 3. Thermogravimetric analysis of bis(acetylacetonato)-ethylenediaminemanganese(II) *in vacuo*. The rate of temperature elevation was fixed at 30°C/hr.

served in the spectrum of the ethylenediamine adduct. It may be due to the structural change from trimeric $Mn(acac)_2$[8] to monomeric $Mn(acac)_2en$. Weak bands at 572 and 516 cm^{-1} in the latter spectrum may be assigned to the metal-nitrogen stretching.

Thermogravimetric analysis, as shown in Fig. 3, indicates that bis(acetylacetonato)ethylenediaminemanganese(II) begins to decompose at around 95°C liberating ethylenediamine, which was trapped at −78°C. The ethylenediamine was transformed to the hydrochloride and identified by the elemental analysis and infrared spectra.[21] Sudden decrease of weight at temperatures above 150°C is due to sublimation of the decomposition residue, which was identified as bis(acetylacetonato)manganese(II) by the elemental analysis and infrared spectra. The weight loss below 150°C amounts to 24% exceeding the calculated value of 19.2% for the ethylenediamine content in this adduct. This discrepancy seems to be caused by partial sublimation of the residual bis-chelate. When a sample was kept at 100°C *in vacuo*, the weight decreased more slowly and reached a constant weight after 6 hr. The weight loss in this case was 22.0% and still higher than the calculated ethylenediamine content.

Molecular weight of $Mn(acac)_2en$ could not be measured on account of insolubility in ether, benzene, and other solvents suitable for the measurement, but it could be presumed to be monomeric from analogy with the bis(allylamine)-adduct which will shortly be described. Magnetic moment of this compound was determined to be 6.08 B.M. by the Gouy method at room temperature. This value is so close to the value of 5.91 B.M. estimated by the spin-only equation that high-spin octahedral configuration of manganese(II) may be proposed for this compound.

Other Primary Amine Adducts with Bis(acetylacetonato)manganese(II). Bis(acetylacetonato)bis(amine)manganese(II) complexes were also prepared by the two types of reactions just as in the case of the ethylenediamine adduct. The 1 : 1 amine adduct was obtained only in a 1 : 1 reaction between bis(acetylacetonato)manganese(II) and allylamine. Even when other primary amines such as propylamine, methallylamine and *trans*-crotylamine were allowed to react with $Mn(acac)_2$ in the mole ratio of one to one, the bis(amine)-adducts were produced exclusively.

TABLE 2. THE NH STRETCHING AND NH_2 BENDING FREQUENCIES OF SEVERAL PRIMARY AMINES AND THEIR ADDUCTS WITH BIS(ACETYLACETONATO)MANGANESE(II) TOGETHER WITH THE C=C STRETCHING FREQUENCIES OF ALLYLIC COMPOUNDS

Compound[a]	$\nu(NH_2)$	$\delta(NH_2)$	$\nu(C=C)$
Ethylenediamine, en	3370 m 3280 m	1592 m, br	
$Mn(acac)_2en$	3278 m 3195 m	~1600	
Propylamine, $PrNH_2$	3385 m 3298 m	1590 m, br	
$Mn(acac)_2(PrNH_2)_2$	3280 w 3200 w, sh	1558 m, sh	
Allylamine, $AllNH_2$	3380 m 3290 m	1595 w, br	1642 m
$Mn(acac)_2(AllNH_2)$	3340 w 3240 w 3160 w	1553 m, sh	1638 w
$Mn(acac)_2(AllNH_2)_2$	3270 w 3200 w, sh	1555 m, sh	1640 w
Methallylamine, $MethallNH_2$	3390 s 3310 s 3190 sh	1595 m, br	1645 m
$Mn(acac)_2(MethallNH_2)_2$	3350 sh 3300 s 3260 m, br	1595 m, br	1645 w
trans-Crotylamine, $CrotNH_2$	3380 m 3300 m 3190 sh	1585 m, br	1655 sh
$Mn(acac)_2(CrotNH_2)_2$	3310 m 3200 w	1600 (?)	1655 sh

a) Free amines as neat liquid and metal complexes in Nujol.

Table 2 summarizes infrared frequencies of NH stretching and NH_2 bending vibrations of these primary amines and their adducts, and those of C=C stretching in allylic amines. The NH stretching frequencies of amine adducts are shifted remarkably to the lower frequency side indicating coordination of amine groups to the metal. Close resemblance of infrared spectra in the lower frequency region as shown in Fig. 2 suggests that the bis-adducts of primary monoamines take the *cis* configuration as is the case for the ethylenediamine adduct. The C=C stretching frequencies of adducts of allylamine and its derivatives show no appreciable shifts from those of free ligands implying nonparticipation of the C=C group in coordination.

Magnetic moments of allylamine, bis-allylamine and bis-propylamine adducts are 5.97, 6.08, and 6.14 B.M.,

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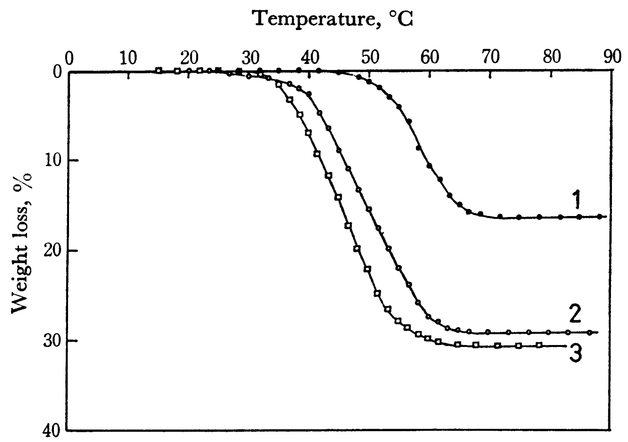

Fig. 4. Thermogravimetric curves for decompositions of amine adducts with bis(acetylacetonato)manganese(II). Curve 1, mono (allylamine)-adduct; curve 2, bis(allylamine)-adduct; curve 3, bis(propylamine)-adduct.

Table 3. Results of thermogravimetric analysis of amine adducts with bis(acetylacetonato)-manganese(II)

Compound	Beginning of decomposition (°C)	Weight loss (%)	Calcd amine content (%)
$Mn(acac)_2en$	95	22.0	19.2
$Mn(acac)_2(AllNH_2)$	45	16.4	18.4
$Mn(acac)_2(AllNH_2)_2$	25	29.1	31.1
$Mn(acac)_2(PrNH_2)_2$	30	30.7	31.8

respectively, indicating that they are all high-spin complexes. Results of thermogravimetric analysis of these compounds are shown in Fig. 4 and Table 3. Allylamine and propylamine adducts decomposed at much lower temperatures than the ethylenediamine adduct did. Thus the weight became constant below 70°C in each case since sublimation of the decomposition residue did not start at these lower temperatures even *in vacuo*.

The volatile product was identified as the free amine, and the decomposition residue as bis(acetylacetonato)-manganese(II) in either case. The observed weight loss in these compounds is close to the calculated amine content, respectively. The higher temperature of decomposition of the ethylenediamine complex seems to reflect its higher thermodynamic stability, compared with bis-adducts of monoamines. However, the trend is independent of the negative shift observed for the N–H stretching frequencies, and might be understood in terms of the entropy effect in the diamine chelate.

The decomposition pressure of the bis(allylamine) complex is higher than that of its mono-adduct and the former compound changes to the latter by prolonged evacuation even at room temperature. The results of molecular weight determination shown in Table 4 indicate that the bis(allylamine) complex is monomeric both in benzene and ether, but the mono(allylamine) complex is dimeric in ether. The latter compound is less soluble in benzene and did not allow the cryoscopic measurement.

Table 4. Molecular weights of allylamine adducts with bis(acetylacetonato)manganese(II)

Compound	Calcd	Found in benzene[a)]	Found in ether[b)]
$Mn(acac)_2(AllNH_2)$	310		580
$Mn(acac)_2(AllNH_2)_2$	367	350	350

a) Cryoscopy
b) Vapor pressure osmometry

Stoichiometry of the Redox Reaction between Tris(acetylacetonato)manganese(III) and Ethylenediamine. A precipitate formed by the reaction between tris(acetylacetonato)manganese(III) and ethylenediamine was identified as bis(acetylacetonato)ethylenediaminemanganese(II) by the elemental analysis and infrared spectra. Since this compound is insoluble in ether at all, the filtrate could be used for the analysis of the excess ethylenediamine, total nitrogen, and liberated acetylacetone as described in the Experimental section.

Table 5. Products of a reaction between tris-(acetylacetonato)manganese(III) and ethylenediamine in ether

	No. of mols	Mol ratio
Reactants employed:		
$Mn(acac)_3$	8.31×10^{-4}	1
ethylenediamine	24.93×10^{-4}	3
Ppt. produced:		
$Mn(acac)_2en$	8.47×10^{-4}	1.02
Contained in the filtrate:		
acetylacetone	6.32×10^{-4}	
bis(acac)ethylenediimine	1.01×10^{-4}	
total acetylacetone	8.34×10^{-4}	1.00
total ethylenediamine	9.30×10^{-4}	1.12
total nitrogen	27.8×10^{-4} g·atom	

As summarized in Table 5 the manganese(II) complex was produced quantitatively. Liberated acetylacetone was also equimolar to the complex, indicating that no appreciable decomposition of the acetylacetonate ligand occurred in this redox reaction. Since 2.493 mmol of ethylenediamine was employed and 0.847 mmol was found as coordinated in the Mn(II) complex, the remaining 1.646 mmol might be expected to exist in the solution. However only 0.930 mmol of ethylenediamine was found in the filtrate existing both as the free diamine and the diimine. Thus 0.716 mmol of the amine must be considered to have been decomposed. Total nitrogen contained in the filtrate was not 2×1.646 mg·atom but only 2.78 mg·atom. These results suggest that ethylenediamine was consumed in reducing Mn(III) to Mn(II). Oxidized products of the amine have not yet been characterized, but some volatile product(s) corresponding to 0.51 mg·atom of nitrogen must have escaped from the reaction mixture during a long period reaction. Thus the over-all redox reaction between tris(acetylacetonato)manganese-(III) and ethylenediamine can be represented by the following equation.

$$Mn(acac)_3 + 2en = Mn(acac)_2en + acacH + \text{decomposition products of en} \quad (1)$$

Discussion

Bis(acetylacetonato)bis(allylamine)manganese(II) was ascertained to be monomeric in benzene and ether. Molecular weights of other bis(monoamine) and ethylenediamine complexes have not been determined, but it may be presumed by analogy that they are all monomeric six-coordinate complexes. Allylamine is quite specific in forming the 1 : 1 adduct which is dimeric in ether and in crystals, too.[22] It is worth noting that the mono-allylamine-adduct is more stable than the bis(allylamine)-adduct while similar mono-adducts of propyl-, methallyl-, and crotyl-amines can not be obtained.

Graddon and Mockler[8] found that 1 : 1 adducts of pyridine and 4-methylpyridine with bis(acetylacetonato)-manganese(II) are both monomeric in benzene and proposed five-coordinate structures for these complexes. On the contrary the present 1 : 1 adduct of allylamine is dimeric and a six-coordinate structure must be considered. As evidenced by the IR data, the ethylenic group of allylamine is not involved in coordination to the metal, and the amine molecule acts as a unidentate ligand. Thus the acetylacetonate groups are considered to take the role of bridging ligands as depicted in Fig. 5. This structure is analogous to that given to dimeric bis(acetylacetonato)aquocobalt(II) by Cotton and Elder,[23] and is the first example of the dimeric manganese(II) complex containing acetylacetonate groups as bridging ligands. It is not certain at the present stage of investigation why propylamine and other monoamines can not assume similar structures, but will be clarified by the X-ray studies now in progress.[22]

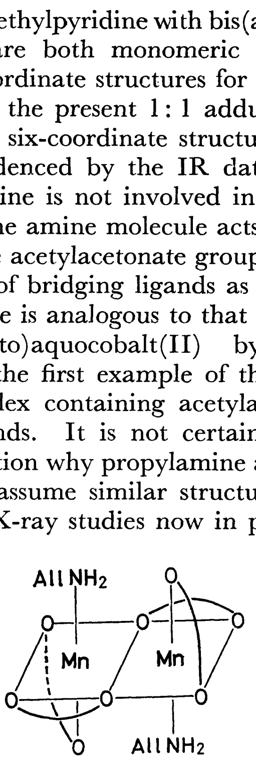

Fig. 5. A proposed structure of dimeric bis(acetylacetonato)-allylaminemanganese(II).

Tris(acetylacetonato)manganese(III) is known as one of the most effective initiators of free-radical polymerization of vinyl monomers.[24] Recently Bamford and Ferrar found that propylenediamine and other donor additives stimulate the radical initiation quite markedly in the polymerizations of styrene, methyl methacrylate and acrylonitrile initiated by Mn(acac)$_3$.[25] The first step of the redox reaction must be coordination of an amine molecule to the manganese(III) metal in such a fashion as represented by Eq. (2), since the outer-sphere electron transfer seems

$$\mathrm{Mn^{III}(acac)_3 + en \longrightarrow (acac)_2Mn^{III}\!<\!\begin{smallmatrix}\mathrm{acac}\\ \mathrm{en}\end{smallmatrix}} \tag{2}$$

less probable. Succeeding steps may be either (3) or (5). If an electron is transferred from the coordinated amine to the metal and the acetylacetonate anion dissociates as a molecule abstracting a proton from neighboring ethylenediamine, there will result the deprotonated ethylenediamine radical (Eq. 3). The product Mn(acac)$_2$ is labile and will add an excess molecule of ethylenediamine quite easily (4) as shown in this paper. On the other hand if an electron is delivered by an acetylacetonate ligand, an acetylacetone radical will be produced (5).

$$\mathrm{(acac)_2Mn^{III}\!<\!\begin{smallmatrix}\mathrm{acac}\\ \mathrm{en}\end{smallmatrix} \longrightarrow}$$

$$\mathrm{Mn^{II}(acac)_2 + C_5H_8O_2 + (en-H)\cdot} \tag{3}$$

$$\mathrm{Mn^{II}(acac)_2 + en \xrightarrow{fast} Mn^{II}(acac)_2en} \tag{4}$$

$$\mathrm{(acac)_2Mn^{III}\!<\!\begin{smallmatrix}\mathrm{acac}\\ \mathrm{en}\end{smallmatrix} \longrightarrow Mn^{II}(acac)_2en + C_5H_7O_2\cdot} \tag{5}$$

$$\mathrm{C_5H_7O_2\cdot + en \xrightarrow{fast} C_5H_8O_2 + (en-H)\cdot} \tag{6}$$

Uehara *et al.*[26] reported that pyridine, α,α′-lutidine, and piperidine accelerated polymerization of styrene, methyl methacrylate, and vinyl acetate initiated by Mn(acac)$_3$, and that polystyrene prepared in the Mn(acac)$_3$-py system showed the carbonyl stretching band at round 1700 cm^{-1} but no absorption due to the pyridine ring. By means of tracer experiments Bamford and Ferrar[27] also disclosed that in the vinyl polymerization initiated by Mn(acac)$_3$ and propylenediamine or dimethyl sulfoxide, each growing radical carried one acetylacetonate residue, but fragments derived from the additives were incorporated in the polymer only to a minor extent. These results indicate unequivocally that the process (5) occurred in the main. As described already acetylacetone molecules are recovered quantitatively in the reaction between Mn(acac)$_3$ and ethylenediamine in the absence of vinyl monomers. The succeeding step (6) must proceed rapidly in advance to spontaneous degradation of the acetylacetone radical.

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