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Some Metal Complexes Containing Ethyl Acetoacetate or Ethyl Malonate as a Neutral Ligand

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The following metal complexes containing ethyl acetoacetate (etacH) or ethyl malonate (etmalH) as a neutral ligand have been prepared: $CoCl_2L$, $CoBr_2L$, $ZnCl_2L$ (L=etacH or etmalH), and $MnBr_2$(etmalH). These compounds are all hygroscopic and unstable, releasing the ester ligand below 100°C *in vacuo* or in donor solvents. The infrared spectra show that the ratio of keto and enol tautomers in etacH complexes is similar to that for the free ligand. The ν(C=O) band attributable to the enol tautomer of etmalH is observed in the complexes, though not in the free ligand. The electronic spectra measured in Nujol suggest that the cobalt(II) complexes are tetrahedral. The structure of $MnBr_2$(etmalH) is not yet certain.

Acetylacetone is one of the most versatile ligand; it usually coordinates to the metal atom as a bidentate anion,[1] although in some cases it serves as a unidentate anion, forming a metal-carbon bond[2] or an ether type metal-oxygen[3] linkage. In a previous paper we reported on several metal complexes containing acetylacetone as a neutral ligand.[4]

The neat liquid of acetylacetone (acacH) is a mixture of keto and enol tautomers; the equilibrium content of the latter was determined by the NMR method to be 81.4% at 25°C.[5] However, in the above metal complexes of neutral acetylacetone, such an equilibrium composition is not maintained; rather, one of the two tautomers is incorporated exclusively. Thus, $MnBr_2(acacH)_2$ involves enolic molecules as unidentate ligands,[6] but $NiBr_2(acacH)_2$,[7] $ZnCl_2$(acacH), CoX_2(acacH), and CrX_2(acac)(acacH) (X=Cl, Br) all contain the keto tautomer as a bidentate ligand.[4] Similarly, $UO_2(acac)_2$(acacH) has been reported to have an enol molecule,[8] and [Ni(acacH)$_3$](ClO_4)$_2$ and other related Ni(II) complexes, the keto tautomer.[9] Proton magnetic resonance studies of $[Mg(acacH)_2(H_2O)_2](ClO_4)_2$ in CD_3NO_2 have also revealed that the keto tautomer is the dominant species bonded to the magnesium ions in solution.[10]

As an extension of the previous work, we have tried to synthesize several metal complexes containing ethyl acetoacetate or ethyl malonate as a neutral ligand. In contrast with acetylacetone, the keto tautomer is the major component in these esters; the enol content has been reported to be about 8% in ethyl acetoacetate[11] and seems to be negligible in ethyl malonate. Thus, it was expected that metal complexes of these ester molecules involve the keto tautomer exclusively.

Experimental

Materials. The anhydrous metal halides were prepared by the following methods. About 50 m*l* of freshly-distilled thionyl chloride was added to 25 g of cobalt(II) chloride hexahydrate, and the mixture was refluxed for about 2 hr. After the vacuum distillation of the excess thionyl chloride, the residual anhydrous cobalt(II) chloride was dried for three days in a vacuum desiccator containing po-

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[1] J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966); E. C. Lingafelter, *Coord. Chem. Rev.*, **1**, 151 (1966).

[2] D. Gibson, *ibid.*, **4**, 225 (1969).

[3] T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *J. Amer. Chem. Soc.*, **92**, 4544 (1970), and references cited therein.

[4] Y. Nakamura, K. Isobe, H. Morita, S. Yamazaki, and S. Kawaguchi, *Inorg. Chem.*, **11**, 1573 (1972).

[5] L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

[6] S. Koda, S. Ooi, H. Kuroya, Y. Nakamura, and S. Kawaguchi, *Chem. Commun.*, **1971**, 280.

[7] S. Koda, S. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, and S. Kawaguchi, *ibid.*, **1971**, 1321.

[8] J. M. Haigh and D. A. Thornton, *Inorg. Nucl. Chem. Lett.*, **6** 231 (1970).

[9] P. W. N. M. van Leeuwen, *Rec. Trav. Chim.*, **87**, 396 (1968); K. Anzenhofer and T. G. Hewitt, *Z. Kristallogr.*, **134**, 54 (1971).

[10] P. W. N. M. van Leeuwen and A. P. Praat, *Inorg. Chim. Acta*, **4**, 101 (1970).

[11] J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

TABLE 1. METAL COMPLEXES CONTAINING ETHYL ACETOACETATE OR ETHYL MALONATE AS A NEUTRAL LIGAND

Complex[a]	Color	Found (Calcd), % M	X	C	H	Magnetic moment BM (°K)
$CoCl_2$(etacH)	pale blue	23.07 (22.67)	26.96 (27.27)	26.59 (27.72)	4.12 (3.88)	5.01 (291)
$CoCl_2$(etmalH)	deep blue	21.17 (20.32)	24.19 (24.45)	28.08 (28.98)	4.12 (4.17)	4.98 (295)
$CoBr_2$(etacH)	light blue	16.19 (16.89)	43.63 (45.81)	22.02 (20.66)	3.30 (2.89)	
$CoBr_2$(etmalH)	deep blue	15.69 (15.55)	41.98 (42.18)	22.06 (22.19)	3.29 (3.19)	4.85 (293)
$MnBr_2$(etmalH)	pale pink	14.64 (14.65)	42.73 (42.63)	22.12 (22.42)	3.31 (3.23)	5.51 (293)
$ZnCl_2$(etacH)	white	24.27 (24.54)	26.56 (26.61)	26.91 (27.05)	3.98 (3.78)	
$ZnCl_2$(etmalH)	white	21.75 (22.05)	24.03 (23.92)	28.11 (28.36)	4.32 (4.08)	

a) etacH: ethyl acetoacetate, $CH_3COCH_2COOC_2H_5$. etmalH: ethyl malonate, $C_2H_5OCOCH_2COOC_2H_5$.

tassium hydroxide.[12] Anal. Found: Co, 45.59; Cl, 54.32%. Commercial zinc(II) chloride was also dried by a similar method to yield an anhydrous compound.[12] Anal. Found: Zn, 47.14; Cl, 52.42%. The anhydrous cobalt(II) bromide was obtained by the dehydration of the commercial hexahydrate by heating at 130°C for 10 hr and by evacuating at the same temperature for 2 hr. Anal. Found: Co, 27.12; Br, 72.61%. The anhydrous manganese(II) bromide was prepared according to Watt and Manhas[13] by a reaction between manganese(II) carbonate and hydrobromic acid. Anal. Found: Mn, 25.48; Br, 74.23%.

Ethyl acetoacetate and ethyl malonate were distilled under reduced pressure, and the distillates, collected at 83—86°C and 99—102°C respectively, were used in this study. Mercury(II) tetraisothiocyanatocobaltate(II) was prepared according to Figgis and Nyholm.[14] Anal. Found: C, 9.73; N, 11.43%. Calcd for $HgCo(NCS)_4$: C, 9.77; N, 11.39%.

Syntheses and Analyses of the Ester Complexes. About a 40-m*l* portion of ethyl acetoacetate or ethyl malonate was added to about 1 g of an anhydrous metal halide, and the mixture was stirred for about 48 hr. The precipitate was filtered, washed with petroleum ether, and dried *in vacuo*. The complexes thus prepared are all hygroscopic; special care was taken to exclude atmospheric moisture in the preparation and filtration procedures.[4]

The cobalt and manganese in these complexes were determined gravimetrically as sulfates, and zinc, as ammonium phosphate. The halide contents were also measured gravimetrically as silver salts. The results of the elemental analysis of these compounds are tabulated in Table 1, together with some properties.

Measurements. No solvent is available in which these complexes are dissolved without decomposition. A solid specimen was ground with Nujol and placed between two plates of opal glass, and its transmission spectrum was measured[15] with a Hitachi-Perkin Elmer 139 spectrophotometer. The infrared spectra were measured in Nujol by means of Hitachi EPI-2 (700—4000 cm^{-1}) and EPI-L (200—700 cm^{-1}) infrared spectrophotometers.

A thermo-spring balance (C–282) of Hamada Denki Seisaku-sho, Ltd., was used for the thermogravimetric analysis of the ethyl malonate complexes; the temperature of a sample was raised at a rate of 20°/hr. The decomposition residue was dissolved in water and analyzed.

The magnetic susceptibility was determined at room temperature by the Gouy method with an automatically-recording magnetic balance of Shimadzu Seisakusho, Ltd. Mercury(II) tetraisothiocyanatocobaltate(II) was used as the reference.

Results

Infrared Spectra. In Table 2 are summarized the infrared absorption spectra of metal complexes of ethyl acetoacetate (etacH) and ethyl malonate (etmalH) in the regions of the carbonyl, metal-oxygen, and metal-halogen stretching vibrations. The carbonyl stretching frequencies of the free ligands were assigned by reference to the literature;[16] they are included in the table. In the infrared spectrum of the free ligand etacH, the $\nu(C=O)$ band for the keto tautomer is very strong and that for the enol tautomer is weak, reflecting the equilibrium composition of the two tautomers. The $\nu(C=O)$ band for the enol tautomer is hardly detectable in the spectrum of etmalH.

The infrared spectra of acetylacetone complexes showed the carbonyl stretching absorption solely due to either the keto or the enol tautomer, revealing that either one of the tautomers was incorporated exclusively in each complex.[4] On the contrary, carbonyl stretching bands attributable to both tautomers are observed in each of the present ester complexes (Table 2), indicating that each compound is a mixture of complex molecules containing the keto tautomer as a ligand and those having the enol tautomer. Although the carbonyl stretching region of these complexes is very broad and exact estimation is difficult, the rough intensity ratio of the carbonyl bands of the two tautomers in each ethyl acetoacetate complex is near to that for the free ligand. This observation suggests that the formation constants of keto and enol complexes are similar in these cases. Since the carbonyl stretching band of the enol tautomer of free ethyl malonate can hardly be identified, it is not certain whether the bands observed at 1618—1658 cm^{-1} for the metal complexes are assignable to the coordinated enol tautomer. If this is indeed the case, though, it must be concluded that the complex formation constant of the enol tautomer is much larger than that

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[12] T. Moeller (ed.), "Inorganic Syntheses," Vol.5, McGraw-Hill, New York (1957), p. 153.

[13] G. W. Watt and B. S. Manhas, *J. Inorg. Nucl. Chem.*, **28**, 1945 (1966).

[14] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1958**, 4190.

[15] K. Shibata, "Methods of Biochemical Analyses," Vol.7 edited by D. Glick, Interscience, New York (1959), p. 77.

[16] W. Gordy, *J. Chem. Phys.*, **8**, 516 (1940); R. S. Rasmussen and R. R. Brattain, *J. Amer. Chem. Soc.*, **71**, 1073 (1949); R. W. Hay and B. P. Caughley, *Aust. J. Chem.*, **20**, 1829 (1967).

TALLE 2. CHARACTERISTIC INFRARED SPECTRA (cm^{-1}) OF METAL COMPLEXES CONTAINING ETHYL ACETOACETATE OR ETHYL MALONATE AS A NEUTRAL LIGAND

L=etacH				L=etmalH					Assignment
L	$CoCl_2L$	$CoBr_2L$	$ZnCl_2L$	L	$CoCl_2L$	$CoBr_2L$	$MnBr_2L$	$ZnCl_2L$	
1738 vs	1717 sh	1720 sh		1750 vs	1750 sh	1755 sh	1753 sh	1737 vs	keto ν(C=O)
1717 vs	1702 vs	1703 vs	1730 vs	1736 vs	1729 vs	1726 vs	1726 vs	1715 vs	
		1685 vs	1706 vs		1698 vs	1690 vs		1683 sh	
1643 m	1657 m	1650 m	1625 m		1657 w	1655 m	1658 m	1618 w	enol ν(C=O)+ν(C=C)
	250	250	233		243			230	ν(M-O)
						235	230		
	242	240	218		232			218	
	343	272	335		340	265	258(?)	330	ν(M-X)
	310	230	300		318	230		305	

of the keto tautomer in the case of ethyl malonate.

Distinct absorption bands appearing in the 377—397 cm^{-1} region were attributed to the metal-oxygen stretching vibrations in the complexes of the keto tautomers. On the other hand, the ν(M–O) bands of the enol tautomers are obscure because of their minor abundances; they will not be assigned here.

The metal-halogen stretching absorptions were assigned according to the literature;[17,18] they are listed in Table 2. These exist in the range of frequencies attributable to the non-bridging metal-halogen stretching vibration in tetrahedral complexes of the MX_2L_2 type, where L respresents a unidentate ligand.

Electronic Spectra and Magnetic Data. The absorption spectra of $CoCl_2$(etacH) and $CoCl_2$(etmalH) in Nujol (Fig. 1) exhibit three maxima, at 600, 675, and 717 nm, and at 598, 680, and 722 nm, respectively. These spectra unequivocally indicate that those are tetrahedral complexes,[19] although their magnetic moments are a little higher than the values usually observed for tetrahedral cobalt(II) complexes.[19]

The observed magnetic moment (5.51 B. M.) of $MnBr_2$(etmalH) certifies that this is a high-spin complex, but we can not distinguish whether it is tetrahedral or octahedral. The absorption spectrum can not be observed by the opal glass method due to the low absorption intensity. However, the pale pink color might reflect an octahedral structure, since manganeses(II) usually has a green-yellow color in tetrahedral environments.[20]

Thermogravimetric Data. The negative shifts of the carbonyl stretching frequencies of etacH and etmalH caused by ligation to metal atoms are minute, suggesting the weakness of these bonds. This is also revealed by the thermogravimetric data of etmalH complexes depicted in Fig. 2 and summarized in Table 3. The zinc complex is most unstable and begins to decompose at 40°C. The weight loss coincides

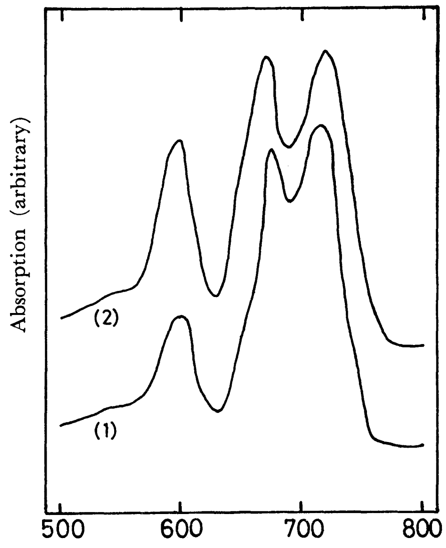

Fig. 1. Absorption spectra of $CoCl_2$(ethyl acetoacetate) (1) and $CoCl_2$(ethyl malonate) (2) in Nujol.

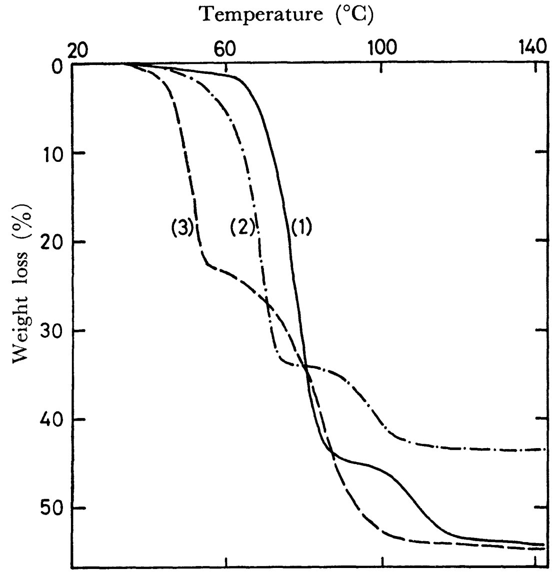

Fig. 2. Thermogravimetric analyses of ethyl malonate (L) complexes: (1) $CoCl_2L$, (2) $MnBr_2L$, (3) $ZnCl_2L$.

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17) R. Colton and J. H. Canterford, "Halides of the First Row Transition Metals," Wiley-Interscience, New York (1969), p. 327.

18) C. Postmus, J. R. Ferraro, A. Quattrochi, K. Shobatake, and K. Nakamoto, *Inorg. Chem.*, **8**, 1851 (1969).

19) R. L. Carlin, "Transition Metal Chemsitry," Vol. 1, Marcel Dekker, New York (1965), p. 1.

20) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed., Interscience, New York (1966), p. 837.

TABLE 3. THERMOGRAVIMETRIC ANALYSIS OF METAL COMPLEXES CONTAINING ETHYL MALONATE AS A NEUTRAL LIGAND

Complex	Beginning of decomposition °C	Wt loss, %		Analysis of residue, %			
				Found		Calcd[b)]	
		Found	Calcd[a)]	M	X	M	X
$CoCl_2$(etmalH)	60	54.07	55.23	45.85	53.96	45.39	54.61
$MnBr_2$(etmalH)	50	42.78	42.72	25.66	74.22	25.58	74.42
$ZnCl_2$(etmalH)	40	54.62	54.03				

a) Calcd for the loss of etmalH. b) Calcd for the anhydrous metal halide.

with the calculated content of the ligand in each complex, while the composition of the residue coincides with that of the metal halide.

Although the final decomposition residue is thus the metal halide, a plateau-like portion is observed in each decomposition curve, suggesting the presence of some metastable intermediate. The composition corresponds to $CoCl_2$: etmalH$=6:1$, $MnBr_2$: etmalH $=5:1$, and $ZnCl_2$: etmalH$=5:3$. Allan *et al.*[21)] studied the thermal decomposition of adducts of cobalt(II) chloride and manganese(II) bromide with pyridine and its methyl derivatives; they found $CoCl_2\cdot 2/3$ py and $MnBr_2\cdot 2/3$(Me-py) as intermediates. Much more effort will be needed to characterize the decomposition intermediates in the present case.

Discussion

In a previous paper acetylacetone complexes were synthesized by three alternative methods:[4)] (1) the direct addition of acetylacetone to anhydrous metal halides, (2) the reaction of the usual acetylacetonate chelate with dry hydrogen bromide in dichloromethane containing free acetylacetone, and (3) the reaction of trichlorotris(tetrahydrofurn)chromium(III) with acetylacetone. The ester complexes were prepared by the first method. In order to succeed in getting solid complexes by this method, the metal halide should have an appropriate solubility in the free ligand. Anhydrous nickel(II) chloride is insoluble in etacH and etmalH, and does not give either complex. On the other hand, the solubility of manganeses(II) bromide in etacH is too high and the isolation of a solid complex was unsuccessful.

The thermodynamic stabilities of ester complexes are relatively low, but those listed in Table 1 were stable enough to be analyzed and characterized. Anhydrous manganese(II) chloride reacted with both etacH and etmalH, giving solid products, but their decomposition pressures were so large that they easily decomposed to the starting materials without affording any complexes of a definite composition. On the contrary, the cobalt(II) bromide complex with etacH held the ligand in excess of the 1 : 1 composition. As is shown in Table 1, even after prolonged evacuation at 50°C the analytical data showed some contamination with the free ligand. The function of the slight excess of etacH in this complex is not at all clear.

As to the structures of these ester complexes, any conclusive discussion is impossible, since no adequate solvent is available for the molecular-weight determination and since no suitable crystal has yet been obtained for the X-ray analysis. The infrared spectra indicate that both the keto and the enol tautomers are incorporated in these ester complexes, while the electronic spectra of solid specimens of cobalt(II) chloride complexes in Nujol suggest the tetrahedral structure for these complexes. The ketonic complex may be presumed to be monomeric, two halogen atoms and two carbonyl oxygen atoms of the keto tautomer surrounding the metal atom tetrahedrally. It is not certain whether the structure of the minor enolic complex is reflected in the absorption spectra. If this is indeed the case, and if the enolic complex also assumes a tetrahedral structure, some polymeric structure containing the Co-Br chain must be formed, since the enol tautomer of etacH or etmalH does not seem to act as a bidentate.

The octahedral structure might be assigned to $MnBr_2$(etmalH) on the basis of its pale pink color. This structure may be realized if the keto tautomer of the ester occupies two adjacent coordination sites and if the $MnBr_2$ unit constructs an infinite spiral chain. On the other hand, two enolic molecules of acetylacetone are used in $MnBr_2(acacH)_2$ to complete the octahedral structure around each manganese atom in the infinite linear $MnBr_2$ chain.[6)] Such a difference in the tautomeric form of the ligand molecule incorporated might be the reason why acetylacetone forms the 2 : 1 complex with $MnBr_2$, while ethyl malonate froms the 1 : 1 complex. Recently Kemula and Iwamoto[22)] investigated the complex formation equilibria in a solution of $SnCl_4$ and various esters. Ethyl acetate, ethyl glutarate, and ethyl adipate act as monodentate ligands and form 1 : 1 and 2 : 1 complexes with $SnCl_4$, depending on the ratio of the ester to $SnCl_4$, but ethyl oxalate and ethyl malonate serve as chelating agents and form only 1 : 1 complexes.

The relative bonding strengths of acacH, etacH, and etmalH to metal might be worth noting. The metal-oxygen stretching frequencies for zinc complexes nearly coincide ($ZnCl_2$(acacH)[4)] 230, 210; $ZnCl_2$(etacH) 233, 218; $ZnCl_2$(etmalH) 230, 218 cm^{-1}), but some difference is noticed for cobalt(II) complexes

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[21)] J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **26**, 1895 (1964); **27**, 1865 (1965).

[22)] A. Kemula and R. T. Iwamoto, *J. Phys. Chem.*, **72**, 1334 (1968).

($CoCl_2$(acacH)[4]) 264, 248; $CoCl_2$(etacH) 250, 242; $CoCl_2$(etmalH) 243, 232 cm^{-1}). The latter results might reflect the relative bonding strengths of these ligands in the order of acacH > etacH > etmalH. The amounts of the nagative shift in the carbonyl stretching frequencies of these complexes from those of free ligands are so small that they do not permit the differentiation of their bonding strengths.

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