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## Several Metal Complexes Containing Acetylacetonate as a Neutral Ligand

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Received September 20, 1971

Several metal complexes containing acetylacetonate as a neutral ligand have been prepared by (1) the direct addition of acetylacetonate to anhydrous metal halides, (2) the reaction of the usual acetylacetonate chelate with dry hydrogen bromide in dichloromethane containing free acetylacetonate, or (3) the reaction of trichlorotris(tetrahydrofuran)chromium(III) with acetylacetonate. Based on the magnetic data and electronic and infrared absorption spectra, structures of these complexes have been proposed:  $\text{CoCl}_2(\text{acacH})$  and  $\text{ZnCl}_2(\text{acacH})$ , tetrahedral;  $\text{MnBr}_2(\text{acacH})_2$ ,  $\text{NiBr}_2(\text{acacH})_2$ ,  $\text{CrBr}_2(\text{acac})(\text{acacH})$ , and  $\text{CrCl}_2(\text{acac})(\text{acacH})$ , octahedral. In the manganese(II) complex enolic molecules of acetylacetonate are coordinated to the metal atom as unidentate ligands, while in all other complexes a ketonic molecule of acetylacetonate is involved as a bidentate ligand.

Pedersen found that copper(II) and other metal ions accelerated the bromination of ethyl acetoacetate and postulated the metal complex of a ketonic ester molecule as an intermediate.<sup>1</sup> However several questions were left to be solved. (1) Can such a complex containing a ketonic molecule really exist? (2) Why are the catalytic activities of the beryllium and aluminum ions negligible in spite of very high stabilities of their enolate chelates of  $\beta$ -dicarbonyl compounds? (3) How does the succeeding rapid reaction of the enolate chelate with bromine proceed?

We have studied the reactions of several metal chelates of acetylacetonate with bromine in dichloromethane and found that products were different according to the nature of the central metal ions. In case of the copper(II) complex with acetylacetonate or ethyl acetoacetate the chelate ring was cleaved, resulting in the  $\gamma$ -brominated diketone and copper(I) bromide or copper(II) bromide depending on the reactants mole ratio.<sup>2</sup> In contrast the quasiaromatic bromination at the  $\gamma$  position of the chelated acetylacetonate occurred in beryllium and aluminum complexes.<sup>3</sup> Such extraordinary stabilities of these metal complexes of  $\gamma$ -bromoacetylacetonate may be the reason that these metal ions are not the effective catalysts for the bromination of  $\beta$ -dicarbonyl compounds.

A novel complex containing an acetylacetonate molecule dibromo(acetylacetonate)cobalt(II) was obtained as an intermediary product in the reaction of tris(acetylacetonato)cobalt(III) with bromine in dichloromethane and was also prepared by the direct addition of acetylacetonate to cobalt(II) bromide.<sup>4</sup> In a quite different way van Leeuwen synthesized  $[\text{Ni}(\text{acacH})_3](\text{ClO}_4)_2$ ,  $[\text{Ni}(\text{acacH})_2(\text{CH}_3\text{COOH})_2](\text{ClO}_4)_2$ , and  $[\text{Ni}(\text{acacH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ .<sup>5</sup> These transition metal complexes containing an acetylacetonate molecule as a ligand strongly support the Pedersen assumption. The present paper reports syntheses and properties of chromium(III), manganese(II), cobalt(II), nickel(II),

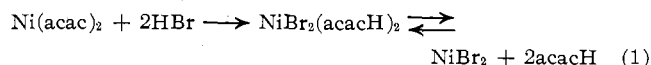
and zinc(II) halide complexes containing acetylacetonate as a neutral ligand.

## Results

**Syntheses.**—Three different methods were employed in synthesizing metal complexes listed in Table I. (1)  $\text{CoCl}_2(\text{acacH})$ ,  $\text{ZnCl}_2(\text{acacH})$ , and  $\text{MnBr}_2(\text{acacH})_2$  were prepared by the direct addition of acetylacetonate to anhydrous metal halides. (2)  $\text{NiBr}_2(\text{acacH})_2$  and  $\text{CrBr}_2(\text{acac})(\text{acacH})$  were obtained by the reactions of dry hydrogen bromide with the usual enolate chelates in dichloromethane containing a large excess of acetylacetonate. (3)  $\text{CrCl}_2(\text{acac})(\text{acacH})$  was derived from  $\text{CrCl}_3(\text{THF})_3$  by the reaction with acetylacetonate.

For the first method to be successful the anhydrous metal halide is desired to be moderately soluble in acetylacetonate. Nickel(II) chloride is practically insoluble in this solvent and does not give an adduct. On the other hand too large solubility is not favorable either. Manganese(II) bromide dissolves in and reacts with ethyl acetoacetate, but the adduct has not yet been isolated as a solid. In the case of manganese(II) chloride and some other metal halides, the solid adduct could be isolated but a constant composition was not attained due to the high decomposition pressure.

The presence of a large excess of acetylacetonate is essential for the second method of preparation. In the absence of the free ligand bis(acetylacetonato)nickel(II) reacts with twice the molar quantity of hydrogen bromide in dichloromethane to give a yellow precipitate of nickel(II) bromide. If acetylacetonate is added to this suspension and stirred for a long time, the yellow precipitate is transformed gradually to a pale green precipitate of  $\text{NiBr}_2(\text{acacH})_2$ . Thus the reaction system is represented by



A large excess of acetylacetonate shifts the equilibrium to the left favoring formation of the complex.

Tris(acetylacetonato)chromium(III) is so stable and substitution inert that it suffers the quasiaromatic substitution even by bromine in organic solvents.<sup>6</sup> However, when more than twice the molar quantity of dry hydrogen bromide was allowed to react with the chelate in dichloromethane containing a large excess of acetyl-

(1) K. J. Pedersen, *Acta Chem. Scand.*, **2**, 252, 385 (1948).(2) Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, **38**, 954 (1965); T. Ogura, Y. Kojima, Y. Nakamura, and S. Kawaguchi, *ibid.*, **38**, 1468 (1965).(3) Y. Nakamura and S. Kawaguchi, *ibid.*, **40**, 1179 (1967); Y. Nakamura, M. Hirata, and S. Kawaguchi, *ibid.*, **40**, 2572 (1967).(4) Y. Nakamura and S. Kawaguchi, *Chem. Commun.*, 716 (1968); Y. Nakamura, M. Gotani, and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, **45**, 457 (1972).(5) P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, **87**, 396 (1968).(6) J. P. Collman, *Advan. Chem. Ser.*, **No. 37**, 78 (1963).

TABLE I  
 METAL COMPLEXES CONTAINING ACETYLACETONE AS A NEUTRAL LIGAND

Compd	Color	Analyses, %								$\mu_{\text{eff}}$ , BM ( $^{\circ}\text{K}$ )
		M		X		C		H		
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$\text{CoCl}_2(\text{acacH})$	Blue	25.63	25.61	30.84	30.86	26.12	25.09	3.51	3.50	4.84 (293)
$\text{ZnCl}_2(\text{acacH})$	White	27.65	27.67	29.99	30.12	25.40	24.88	3.41	3.48	
$\text{MnBr}_2(\text{acacH})_2$	Pale pink	13.24	13.33	38.51	38.41	28.93	28.47	3.89	3.96	6.14 (297)
$\text{NiBr}_2(\text{acacH})_2$	Pale green	14.02	14.11	38.16	37.22	28.66	28.13	3.82	3.83	3.39 (295)
$\text{CrBr}_2(\text{acac})(\text{acacH})$	Pale green			38.87	38.35	29.22	29.20	3.68	4.15	3.61 (293)
$\text{CrCl}_2(\text{acac})(\text{acacH})$	Pale green			22.01	21.69	37.56	37.40	4.69	4.76	3.96 (293)

TABLE II

CHARACTERISTIC INFRARED SPECTRA ( $\text{cm}^{-1}$ ) OF METAL COMPLEXES CONTAINING ACETYLACETONE AS A NEUTRAL LIGAND									Assignment
acacH (L)	$\text{CoCl}_2\text{L}$	$\text{CoBr}_2\text{L}^a$	$\text{ZnCl}_2\text{L}$	$\text{NiBr}_2\text{L}_2$	$\text{CrCl}_2(\text{acac})\text{L}$	$\text{CrBr}_2(\text{acac})\text{L}$	$\text{MnBr}_2\text{L}_2$		
1730	1727 sh	1720 sh		1729 sh	1739 sh				Keto $\nu(\text{C}=\text{O})$
1712	1703	1705	1715	1693	1692	1680			
1630							1627		Enol $\nu(\text{C}=\text{O})$ Enol $\nu(\text{C}=\text{C})$
						1560	1564		
						1528			Chelate $\nu(\text{C}=\text{O})$ Chelate $\nu(\text{C}=\text{C})$
						479	475		
	264	260 sh	230		398	398			$\nu(\text{M}-\text{O})$
	248	(234)	210	237	335	335	185		
	347	272	338	178	385	330	148 sh		$\nu(\text{M}-\text{X})$
	315	234	304		375		138		

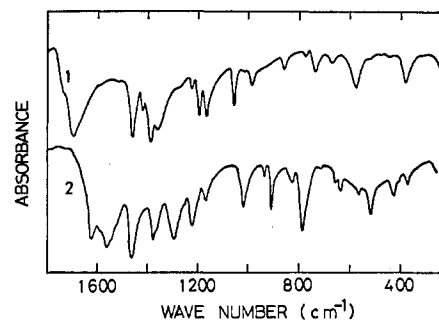
<sup>a</sup> From ref 4.

acetone, one of the three chelate rings was broken liberating one molecule of acetylacetonate, and a proton was added to the  $\gamma$  position of another acetylacetonate ligand resulting in  $\text{CrBr}_2(\text{acac})(\text{acacH})$ .

The third method of preparation is interesting. The direct reaction of acetylacetonate with anhydrous chromium(III) chloride does not give a complex containing acetylacetonate molecules but produces the normal enolate chelate liberating hydrogen chloride. However, when trichlorotris(tetrahydrofuran)chromium(III) was dissolved in acetylacetonate, only an equimolar amount of hydrogen chloride was evolved resulting in  $\text{CrCl}_2(\text{acac})(\text{acacH})$ . The mechanism of this mild reaction is not clear at all, but there might be involved the formation of an intermediary compound  $\text{CrCl}_2(\text{acac})(\text{THF})_2$  followed by the substitution of THF ligands by an acetylacetonate molecule.

Six complexes prepared in this study are summarized in Table I. All these complexes are hygroscopic and rather thermodynamically unstable. No inert solvent is available for the molecular weight determination. Absorption spectra of some compounds were observed in acetylacetonate solutions and those of the others were measured in Nujol mull.

**Infrared Spectra.**—Ir data of the present complexes in the regions of carbonyl, metal-oxygen, and metal-halogen stretching vibrations are listed in Table II, and absorption curves of two representative complexes,  $\text{NiBr}_2(\text{acacH})_2$  and  $\text{MnBr}_2(\text{acacH})_2$ , are reproduced in Figure 1. Cobalt(II), zinc(II), and nickel(II) complexes show the carbonyl stretching absorption at around  $1700\text{ cm}^{-1}$  indicating involvement of the ketonic molecule of acetylacetonate.<sup>7</sup> Chromium(III) complexes show two kinds of the carbonyl stretching vibrations. The  $1692\text{-}$  or  $1680\text{-cm}^{-1}$  peak is again assignable to the ketonic molecule, and bands at  $1560\text{-}1517\text{ cm}^{-1}$  are attributed to the  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$


 Figure 1.—Infrared absorption spectra in the  $1750\text{-}250\text{-cm}^{-1}$  region of  $\text{NiBr}_2(\text{acacH})_2$  (curve 1) and  $\text{MnBr}_2(\text{acacH})_2$  (curve 2) in Nujol.

stretching of the chelated acetylacetonate group.<sup>8</sup> In contrast with these complexes dibromobis(acetylacetonate)manganese(II) revealed absorption bands at  $1627$  and  $1564\text{ cm}^{-1}$  suggesting that both of the two acetylacetonate molecules involved are of the enol form.

Frequencies of the  $\text{M}-\text{O}$  stretching vibrations in the present complexes of neutral acetylacetonate are expected to be lower than those observed for usual enolate chelates since the metal-ligand bonding in the former should be weaker than that in the latter. The chromium(III) complexes contain both an acacH molecule and an acac anion linked to the same metal atom and enable a direct comparison of these two ligands. Mikami, Nakagawa, and Shimanouchi measured far-infrared spectra of several divalent and trivalent metal chelates of acetylacetonate and performed a rigorous normal-coordinate analysis to clarify the vibrational assignments.<sup>9</sup> More recently Nakamoto, Udovich, and Takemoto reported the metal isotope effect on metal-ligand vibrations in several acetylacetonate com-

(7) R. Mecke and E. Funck, *Z. Elektrochem.*, **60**, 1124 (1956); E. E. Ernstbrunner, *J. Chem. Soc. A*, 1558 (1970).

(8) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed. Wiley-Interscience, New York, N. Y., 1970, p 247.

(9) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, **23**, 1037 (1967).

plexes.<sup>10</sup> According to these papers 460- and 354-cm<sup>-1</sup> peaks observed for Cr(acac)<sub>3</sub> are assigned to the Cr-O stretching vibrations. Spectra of CrX<sub>2</sub>(acac)(acacH) are very similar to that of Cr(acac)<sub>3</sub>, and 479- and 398-cm<sup>-1</sup> bands of the chloro complex and 475- and 398-cm<sup>-1</sup> bands of the bromo complex are assignable to the Cr-O(acac) vibrations. Novel strong peaks observed at 335 cm<sup>-1</sup> for both complexes might be attributable to the Cr-O(acacH) stretching. Thus frequency of the Cr-O stretching in the molecular ligand is lower by 140 cm<sup>-1</sup> than that in the corresponding anionic ligand. The metal isotope effect on the far-infrared absorption bands of the monomeric complex Ni(acac)<sub>2</sub>(py)<sub>2</sub> was also reported by Nakamoto, *et al.*,<sup>10</sup> and the 274-cm<sup>-1</sup> band was assigned to a pure Ni-O stretching mode. NiBr<sub>2</sub>(acacH)<sub>2</sub>, on the other hand, shows a very strong peak at 237 cm<sup>-1</sup>, which may be attributed to the  $\nu$ (Ni-O) vibration. The Mn-O stretching absorption for MnBr<sub>2</sub>(acacH)<sub>2</sub> is observed at 185 cm<sup>-1</sup>.

Two strong bands at 264 and 248 cm<sup>-1</sup> observed for CoCl<sub>2</sub>(acacH) and those at 230 and 210 cm<sup>-1</sup> for ZnCl<sub>2</sub>(acacH) may be assigned to the Co-O and Zn-O stretching, respectively. The  $\nu$ (M-O) vibrations of the Co(II) complexes lie about 30 cm<sup>-1</sup> above those of the comparable Zn(II) complexes, as is the case for the  $\nu$ (M-N) vibrations of tetrahedral MX<sub>2</sub>(py)<sub>2</sub> complexes.<sup>11</sup> The corresponding Co-O bands for CoBr<sub>2</sub>(acacH) are obscured by the  $\nu$ (Co-Br) absorptions at 272 and 234 cm<sup>-1</sup>. One Co-O band appears as a shoulder at 260 cm<sup>-1</sup>, and the other band might be hidden by a very strong Co-Br peak at 234 cm<sup>-1</sup>.

The infrared spectra of CrCl<sub>2</sub>(acac)(acacH) and CrBr<sub>2</sub>(acac)(acacH) in the 700-100-cm<sup>-1</sup> region are very similar to each other except that the former shows two strong peaks at 385 and 375 cm<sup>-1</sup>, while the latter shows a single peak at 330 cm<sup>-1</sup>. They could be assigned to the  $\nu$ (Cr-Cl) and  $\nu$ (Cr-Br) vibrations, respectively. The strong bands at 347 and 315 cm<sup>-1</sup> observed for CoCl<sub>2</sub>(acacH) and not for CoBr<sub>2</sub>(acacH) were similarly assigned to the Co-Cl stretching. Recently Nakamoto and his coworkers<sup>12</sup> studied the cobalt(II)-halogen stretching vibrations of CoX<sub>2</sub>L<sub>2</sub> type complexes (L = py, 4-Cl(py), or 4-Br(py)) and found that the bridging Co-Cl stretching vibrations in the polymeric octahedral form occurred in the 155-186-cm<sup>-1</sup> region, while the terminal Co-Cl stretching vibrations in the monomeric tetrahedral form were found in the 306-347-cm<sup>-1</sup> region. The observed absorptions of CoCl<sub>2</sub>(acacH) at 347 and 315 cm<sup>-1</sup> well conform to the supposition that this compound is composed of monomeric tetrahedral molecules containing terminal chloride ions. The strong bands observed at 272 and 234 cm<sup>-1</sup> for CoBr<sub>2</sub>(acacH) were attributed to the  $\nu$ (Co-Br) vibrations and are very close to  $\nu$ (Co-Br) in the tetrahedral CoBr<sub>2</sub>(py)<sub>2</sub>.<sup>11</sup> The lower frequency peak is stronger than the other due to overlapping of the  $\nu$ (Co-Br)/ $\nu$ (Co-Cl) ratios are 0.78 and 0.74 in this case. The  $\nu$ (Zn-Cl) absorptions appear at 338 and 304 cm<sup>-1</sup>.

The far-infrared spectrum of NiBr<sub>2</sub>(acacH)<sub>2</sub> was compared with that of *trans*-NiBr<sub>2</sub>(py)<sub>4</sub>.<sup>11</sup> The  $\nu$ (Ni-

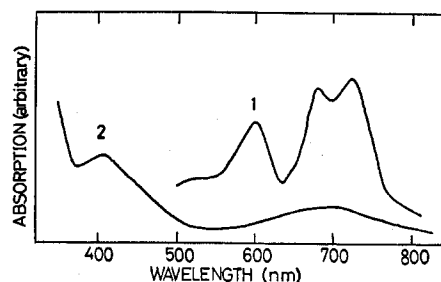


Figure 2.—Absorption spectra of solid CoCl<sub>2</sub>(acacH) (curve 1) and NiBr<sub>2</sub>(acacH)<sub>2</sub> (curve 2) in Nujol.

O) and  $\nu$ (Ni-N) vibrations occur at the same frequencies (237 cm<sup>-1</sup>) in these complexes. However, the  $\nu$ (Ni-Br) frequencies are different, and the peak at 178 cm<sup>-1</sup> for NiBr<sub>2</sub>(acacH)<sub>2</sub> seems assignable to the  $\nu$ (Ni-Br) vibration.

Recently Goldstein and Unsworth<sup>13</sup> determined the metal-halogen stretching modes in several polymeric octahedral bis-pyridine complexes of bivalent metal halides and assigned the 147- and 135-cm<sup>-1</sup> bands to the Mn-Br stretching. MnBr<sub>2</sub>(acacH)<sub>2</sub> is an analog of MnBr<sub>2</sub>(py)<sub>2</sub> and exhibits the  $\nu$ (Mn-Br) vibrations at 148 (sh) and 138 cm<sup>-1</sup>.

**Electronic Spectra.**—As shown in Figure 2 a solid specimen of CoCl<sub>2</sub>(acacH) in Nujol gave an absorption spectrum characteristic of the tetrahedral cobalt(II) complex,<sup>14</sup> exhibiting absorption maxima at 720, 680, and 595 nm. The absorption spectrum of this compound in an acetylacetonate solution is similar to that at a solid state except that the lowest energy peak (720 nm) is lost in the latter. A similar behavior has also been observed for CoBr<sub>2</sub>(acacH), but the reason is not clear as yet. A visible absorption spectrum of NiBr<sub>2</sub>(acacH)<sub>2</sub> was also measured in Nujol (Figure 2). Two absorption maxima at 695 and 405 nm indicate that the nickel atom lies in an octahedral environment.

Figure 3 shows an absorption spectrum of CrCl<sub>2</sub>-

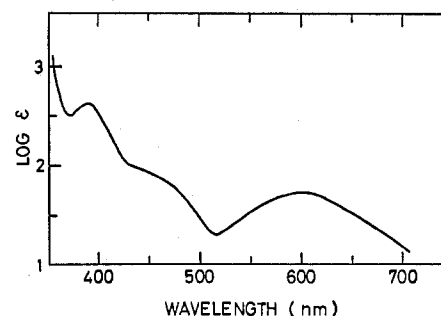


Figure 3.—An absorption spectrum of CrCl<sub>2</sub>(acac)(acacH) in acetylacetonate.

(acac)(acacH) in acetylacetonate. Two maxima at 600 and 395 nm and a shoulder at 450 nm are observed. A solid specimen exhibits a similar spectrum in Nujol, but absorption maxima are shifted to the longer wavelength side: 650, 470 (sh), and 420 nm. CrBr<sub>2</sub>(acac)(acacH) also shows a spectrum similar to that of the chloro complex. These spectral data reveal that both chromium(III) complexes have the octahedral structure.

(10) K. Nakamoto, C. Udovich, and J. Takemoto, *J. Amer. Chem. Soc.*, **92**, 3973 (1970).

(11) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(12) C. Postmus, J. R. Ferraro, A. Quattrocchi, K. Shobatake, and K. Nakamoto, *ibid.*, **8**, 1851 (1969).

(13) M. Goldstein and W. D. Unsworth, *Inorg. Nucl. Chem. Lett.*, **6**, 25 (1970); *Inorg. Chim. Acta*, **4**, 342 (1970).

(14) R. L. Carlin, *Transition Metal Chem.*, **1**, 1 (1965).

**Magnetic Moments.**—Magnetic moments of the present complexes are included in Table I. The value 6.14 BM for  $\text{MnBr}_2(\text{acacH})_2$  indicates that this is a high-spin octahedral complex.  $\text{NiBr}_2(\text{acacH})_2$  also shows a probable value of a magnetic moment as an octahedral complex. The value 4.84 BM of  $\text{CoCl}_2(\text{acacH})$  is much larger than 4.25 BM for the corresponding bromo complex,  $\text{CoBr}_2(\text{acacH})$ ,<sup>4</sup> and exceeds the usual values of 4.4–4.7 BM reported for tetrahedral cobalt(II) complexes.<sup>14</sup> However, the absorption spectra of these compounds described above support the tetrahedral structure unequivocally and the possibility of the octahedral environment must be denied.  $\text{CrCl}_2(\text{acac})(\text{acacH})$  shows an appropriate value of 3.96 BM as an octahedral complex, but  $\text{CrBr}_2(\text{acac})(\text{acacH})$  has a lower value of 3.61 BM. The reason for this discrepancy is not clear.

**Thermogravimetric Data.**—The present complexes involve acetylacetonate as a neutral ligand and its linkage to the central metal atom must be weaker than that of an enolate anion. This situation is clearly reflected by both the positive shift of  $\nu(\text{C}=\text{O})$  and the negative shift of  $\nu(\text{M}-\text{O})$  in comparison with those for the usual enolate chelates. To confirm this supposition further, thermogravimetric analyses have been performed. As illustrated in Figure 4 the nickel(II) complex began to

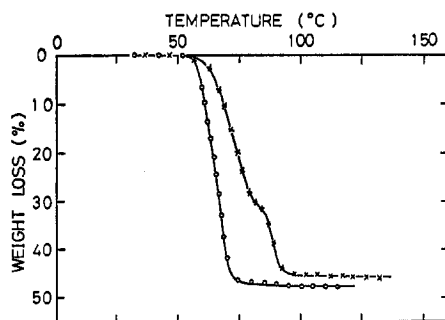


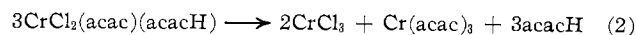
Figure 4. The thermogravimetric analyses of  $\text{NiBr}_2(\text{acacH})_2$  (O) and  $\text{MnBr}_2(\text{acacH})_2$  (X) at the heating rate of 20 and 30°/hr, respectively.

decompose at around 55° liberating two molecules of acetylacetonate, which was collected in a trap cooled by Dry Ice-methanol and identified by the gas chromatography. The observed weight loss of 48% exactly coincides with the calculated value, and the decomposition residue was analyzed to be nickel(II) bromide. *Anal.* Found: Ni, 26.89; Br, 72.40.

The pyrolysis curve of  $\text{MnBr}_2(\text{acacH})_2$  started at around 40° and showed a shoulder at around 80°, but it is not so distinct as to discriminate between the two molecules of acetylacetonate. The observed total weight loss up to 100° amounted to 46% which was near to the calculated value, 48%. Decomposition products were again identified to be acetylacetonate and manganese(II) bromide. *Anal.* Found: Mn, 25.09; Br, 70.30. Thermal decompositions of  $\text{CoCl}_2(\text{acacH})$  and  $\text{ZnCl}_2(\text{acacH})$  were not studied, but similar behaviors may be observed as the case of  $\text{CoBr}_2(\text{acacH})$ .<sup>4</sup>

It was anticipated that the chromium(III) complex might be transformed to a binuclear species upon liberation of acetylacetonate. However, this was not realized, but a decomposition product was sublimed and identified to be tris(acetylacetonato)chromium(III). A dis-

proportionation reaction such as eq 2 must have occurred.



**Structures of Acetylacetonate Complexes.**—Physical properties, especially electronic and infrared spectra of the present complexes, afford unequivocal evidences for the structural assignments depicted in Figure 5. Cobalt-

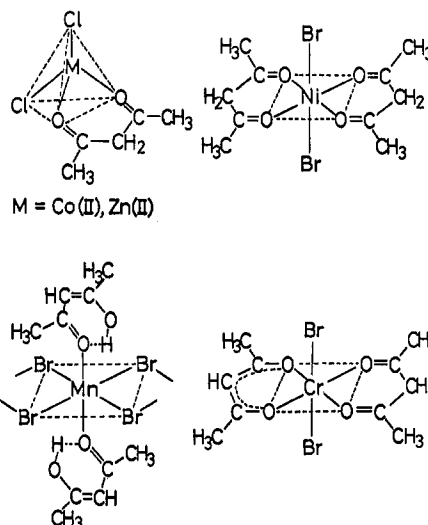


Figure 5.—Proposed structures of metal complexes containing acetylacetonate as a neutral ligand.

(II) complexes have the tetrahedral structure containing a ketonic molecule of acetylacetonate. The zinc(II) complex also involves the keto tautomer and is supposed to take the tetrahedral structure.

Manganese(II) and nickel(II) complexes are both octahedral but the tautomeric form of acetylacetonate molecules is different. The infrared data definitely indicate that the manganese(II) complex contains enolic molecules while the nickel(II) complex contains ketonic molecules. These two types of bonding have in fact been established by the X-ray analysis. In a crystal of  $\text{MnBr}_2(\text{acacH})_2$  the manganese and bromine atoms constitute an infinite chain  $(\text{MnBr}_2)_\infty$  and two enolic acetylacetonate molecules are linked to each metal atom as unidentate ligands, thus constructing the octahedral arrangement of  $[\text{MnBr}_2\text{O}_2]$ .<sup>15</sup> On the other hand, a crystal of  $\text{NiBr}_2(\text{acacH})_2$  is composed of a discrete molecule of *trans*-dibromobis(acetylacetonate)nickel(II) which forms a tetragonally distorted octahedron.<sup>16</sup>

On the basis of visible and infrared spectra the chromium(III) complexes are supposed to have an octahedral structure containing both an acetylacetonate anion and a ketonic molecule. The fact that  $\text{CrBr}_2(\text{acac})(\text{acacH})$  exhibits only one Cr-Br stretching band seems to provide strong evidence for its *trans* geometry. On the other hand there remains some uncertainty concerning the configuration of  $\text{CrCl}_2(\text{acac})(\text{acacH})$ , since two strong peaks are observed in the  $\nu(\text{Cr}-\text{Cl})$  region although the general pattern of its infrared spectrum in the region below  $700\text{ cm}^{-1}$  shows a close resemblance to that of the bromo complex suggesting the same geometry with the latter.

(15) S. Koda, S. Ooi, H. Kuroya, Y. Nakamura, and S. Kawaguchi, *Chem. Commun.*, 280 (1971).

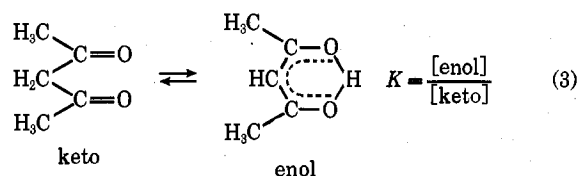
(16) S. Koda, S. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, and S. Kawaguchi, *ibid.*, 1321 (1971).

### Discussion

We have tried to prepare the first transition metal complexes of molecular acetylacetonone and obtained Cr(III), Mn(II), Co(II), and Ni(II) complexes so far. It is very interesting that Cr(III) formed dihalogeno complexes involving both an acetylacetonone molecule and its anion, and the other three divalent metal ions gave complexes of different structures. NiBr<sub>2</sub>(acacH)<sub>2</sub> consists of monomeric octahedral molecules, while cobalt(II) does not give a stable octahedral bis-acetylacetonone complex but affords a tetrahedral complex, CoX<sub>2</sub>(acacH). This is in accord with the general understanding that tetrahedral complexes of cobalt(II) are relatively stable while those of nickel(II) are not.<sup>17</sup>

Both the manganese(II) and cobalt(II) bromides adopt the cadmium(II) iodide structure, and cobalt(II) chloride and nickel(II) bromide adopt the similar cadmium(II) chloride structure. By the reactions of cobalt(II) and nickel(II) halides with acetylacetonone the crystal lattice is broken and discrete complex molecules result. The stabilization energy afforded by complex formation seems to overcome the lattice energy in these cases. On the contrary MnBr<sub>2</sub>(acacH)<sub>2</sub> maintains the polymeric -MnBr<sub>2</sub>- chain, suggesting the insufficient stabilization by ligation of acetylacetonone. This discrepancy might be due to the absence of the ligand field stabilization effect in the latter case of a d<sup>5</sup> metal.

It is well known that acetylacetonone consists of keto and enol tautomers. Burdett and Rogers<sup>18</sup> determined the equilibrium constant *K* (see eq 3) of pure acetylacetonone by the nmr method to be 4.3 at 33°. The



stabilization of the enol tautomer (81% at 33°) is brought about mainly by the intramolecular hydrogen bonding and further by the electron delocalization. In solutions of acetylacetonone the tautomeric equilibrium is shifted according to the nature of solvent. Nonpolar aprotic solvents such as benzene and ether are favorable for the enol tautomer, while dipolar protic solvents such as water and methanol stabilize the keto tautomer.<sup>19</sup>

Except for the manganese(II) complex, all other complexes of acetylacetonone now prepared contain the keto tautomer exclusively. Previously reported compounds containing neutral acetylacetonone, MoOCl<sub>3</sub>(acacH),<sup>20</sup> SnCl<sub>4</sub>(acacH),<sup>21</sup> TiCl<sub>4</sub>(acacH),<sup>21</sup> and [Ni(acacH)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, all involve ketonic molecules, too. [Mg(acacH)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> has also been reported to have the keto tautomer as predominant species even in a nitromethane solution.<sup>22</sup> It is quite natural that the polar structure of the keto tautomer is preferable for metal coordination

to the stabilized cyclic structure of the enol tautomer. The chelate formation must further stabilize the resultant complexes.

Coordination of the enol tautomer to manganese(II) as a unidentate ligand looks like an exception. The isolated coordination sites located above and below the polymeric -MnBr<sub>2</sub>- plane might force the metal atom to adopt the enol tautomer as a unidentate ligand. Only one other example of this linkage mode has been reported by Haigh and Thornton.<sup>23</sup> UO<sub>2</sub>(acac)<sub>2</sub>(acacH) was presumed to have a pentagonal-bipyramidal structure. Two oxide anions occupy the apical positions and two chelate rings of acetylacetonate anions constitute the equatorial plane. The seventh isolated coordination site accepts the enol tautomer of acetylacetonone. Many more examples are desirable to examine the present presumption.

### Experimental Section

**Materials.**—About 50 ml of freshly distilled thionyl chloride was added to about 25 g of cobalt(II) chloride hexahydrate. After refluxing of the mixture for about 2 hr, excess thionyl chloride was distilled away and resulting anhydrous cobalt(II) chloride was kept for 3 days in a vacuum desiccator containing potassium hydroxide.<sup>24</sup> Anal. Found: Co, 45.59; Cl, 54.32. Anhydrous zinc chloride was also prepared by a similar method.<sup>24</sup> Anal. Found: Zn, 47.14; Cl, 52.42. Anhydrous manganese(II) bromide was prepared by the reaction of manganese(II) carbonate with hydrobromic acid according to the method of Watt and Manhas.<sup>25</sup> Anal. Found: Mn, 25.59; Br, 74.34. Anhydrous chromium(III) chloride was manufactured by Yakuri Chemicals Co., Ltd., and used without further purification.

Acetylacetonone was supplied by Daicel Co., Ltd., and distilled before use. Dichloromethane was purified according to the standard method.<sup>2</sup> Dry hydrogen bromide was prepared by the reaction of tetralin with bromine and dissolved in dichloromethane.<sup>8</sup> Tetrahydrofuran was dried with potassium hydroxide and distilled over sodium. Petroleum ether (bp 40–70°) was also distilled over sodium.

Mercury(II) tetraisothiocyanatocobaltate(II) was prepared according to Figgis and Nyholm<sup>26</sup> and used as a reference substance for magnetic measurements. Bis(acetylacetonato)nickel(II) was obtained by dehydration at 100° *in vacuo* for 4 hr of bis(acetylacetonato)diaquanickel(II) which was prepared by the method of Charles and Paulikowski<sup>27</sup> and recrystallized three times from methanol. Anal. Found: Ni, 22.82; C, 46.23; H, 5.54. Tris(acetylacetonato)chromium(III) was prepared according to Fernelius and Blanch<sup>28</sup> and recrystallized from benzene. Anal. Found: C, 51.68; H, 6.06.

**Syntheses of Novel Complexes. Dichloro(acetylacetonone)cobalt(II), CoCl<sub>2</sub>(acacH).**—About 40 ml of acetylacetonone was added to about 1 g of anhydrous cobalt(II) chloride in a small round-bottom flask, which was stoppered and agitated magnetically. Cobalt(II) chloride was dissolved gradually and at the same time the amount of the other precipitate increased. About 48 hr was necessary for completion of the reaction.

**Dichloro(acetylacetonone)zinc(II), ZnCl<sub>2</sub>(acacH), and Dibromobis(acetylacetonone)manganese(II), MnBr<sub>2</sub>(acacH)<sub>2</sub>.**—Both complexes were prepared by the similar method as that for the cobalt(II) complex.

**Dibromobis(acetylacetonone)nickel(II), NiBr<sub>2</sub>(acacH)<sub>2</sub>.**—One gram (4 mmol) of bis(acetylacetonato)nickel(II) was dissolved in 30 ml of dichloromethane containing 18 g (180 mmol) of acetylacetonone in a three-necked flask equipped with a buret, a glass tube containing phosphorus pentoxide, and a glass tube to be used for delivery of the reaction mixture. From the buret about 50 ml of a dichloromethane solution containing 8 mmol of

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dry hydrogen bromide was added dropwise with stirring. The green color of the initial solution lightened gradually while a pale green precipitate increased.

**Dibromo(acetylacetonato)(acetylacetonato)chromium(III), Cr-Br<sub>2</sub>(acac)(acacH).**—In a similar fashion as above 1.5 g (4.3 mmol) of tris(acetylacetonato)chromium(III) was dissolved in dichloromethane containing 20 g (200 mmol) of acetylacetonate and allowed to react with 25.8 mmol of dry hydrogen bromide in dichloromethane. The reaction mixture was kept standing overnight to increase the amount of the pale green precipitate.

**Dichloro(acetylacetonato)(acetylacetonato)chromium(III), CrCl<sub>2</sub>(acac)(acacH).**—According to the literature,<sup>29</sup> except for exclusion of zinc powder, anhydrous chromium(III) chloride was allowed to react with dry tetrahydrofuran in a Soxhlet extractor to produce trichlorotris(tetrahydrofuran)chromium(III). About 1 g of the purple complex CrCl<sub>3</sub>(THF)<sub>3</sub> was dissolved in about 8 ml of acetylacetonate. Hydrogen chloride gas was evolved resulting in a dark green solution, to which about 30 ml of dry petroleum ether was added to separate CrCl<sub>2</sub>(acac)(acacH) as a pale green precipitate.

All these novel complexes are very hygroscopic and were transferred from the reaction vessel *via* polyethylene tubing to a filtration apparatus set up in a desiccator containing phosphorus pentoxide. They were washed with petroleum ether and dried *in vacuo*.

**Analyses and Measurements.**—Metal contents in these complexes were determined gravimetrically: cobalt and manganese as sulfates, nickel as the bis(dimethylglyoximate) complex, and zinc as ammonium phosphate. Halogens were also determined gravimetrically as silver salts.

Absorption spectra of solutions were obtained using a Hitachi

EPS-3T recording spectrophotometer. A solid specimen was ground with Nujol and placed between two plates of opal glass, and its transmission spectrum was measured<sup>30</sup> with a Hitachi Perkin-Elmer spectrophotometer, Model 139. The infrared spectra of solid specimens were measured in Nujol by means of Hitachi EPI-2 (4000–700 cm<sup>-1</sup>), EPI-L (700–200 cm<sup>-1</sup>), and FIS-3 (400–30 cm<sup>-1</sup>) infrared spectrophotometers.

A C-282 Thermo-Spring balance of Hamada Denki Seisakusho, Ltd., was used for the thermogravimetric analysis, and the temperature of a sample was raised at a rate of 20 or 30°/hr *in vacuo*. The volatile decomposition product was collected in a trap cooled with Dry Ice-methanol and submitted to the gas chromatographic analysis. A column of Apiezon L grease carried on Neosorb NC (Nishio Industries Co., Ltd.) was employed at 100° on which hydrogen gas was passed at a flow rate of 40 cm<sup>3</sup>/min. On the other hand, the solid 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 (Shimadzu Seisakusho Co., Ltd.). The sample was put into a tube (3 mm in diameter and 20 mm in length) quickly. Hexaamminechromium(III) chloride and mercury(II) tetraisothiocyanatocobaltate(II) were used as reference compounds.

**Acknowledgments.**—We are indebted to Dr. Hanako Kobayashi of Kyoto University for her help in magnetic measurements and also to Mr. J. Gohda for the elemental analyses. Financial aid by the Ministry of Education and kind supply of acetylacetonate by Daicel Co., Ltd., are also acknowledged.

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## Phthalocyanine Derivatives from 1,2,4,5-Tetracyanobenzene or Pyromellitic Dianhydride and Metal Salts

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Received September 15, 1971

Two general methods have been reported for the preparation of fused-ring polymeric phthalocyanines. These preparations involve the reaction of tetrafunctional benzene [1,2,4,5-tetracyanobenzene (TCB) or pyromellitic dianhydride (PMDA)] with metal salts, so that the ideal products of such reactions would be sheet-type polymers in which each benzene ring is fused into two phthalocyanine rings. The products of the above reactions now have been investigated. It has been found that (1) the work-up procedures described in the literature for the reactions do not produce pure compounds; (2) the pure compounds which were produced in the present investigation from the reaction of TCB with metal salts are monomeric phthalocyanine derivatives with imide or carboxylic functional groups on the available peripheral sites; (3) the products of the reaction using PMDA are polymeric phthalocyanines, but they are quite impure and probably have only imide functional groups on the peripheral positions rather than carboxylic acid groups as previously described. In the procedure by which the structural assignments were made in this work, hydrolysis derivatives of the complexes are first prepared (thus converting all imide functional groups to carboxylic acid groups); then each complex and its hydrolysis derivative are compared by means of their elemental analyses and infrared spectra. The structures may be inferred by interpretation of these comparative data.

### Introduction

The polymeric phthalocyanines have attracted a good deal of attention in recent years. Work in this area has evolved along three principal structural themes. The first (and more common) type of polymer involves the bridging of phthalocyanine units by exocyclic groups attached to the benzene rings (Figure 1a). The second type is one in which a single benzene ring is fused into two phthalocyanine cycles<sup>1,2</sup> (Figure 1b).

In a third type, the central metal ions are bridged by oxygen atoms to form the polymeric linkages.<sup>3,4</sup> This gives a stacked polymer rather than a sheet polymer.

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