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Cobalt(II) Complexes Containing Diacetylacetone and Its Thio Derivative

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The complex compounds of many metal ions containing β-diketones have already been synthesized and studied.1,2) The metal complexes of thio-derivatives of β-diketones were reported first by Martin and Stewart.3)

These thio-β-diketonates were obtained by passing hydrogen chloride and hydrogen sulfide through ethanol solutions containing acetylacetone and metal halide because of the difficulty of the isolation of dithioacetylacetone, which has a tendency to dimerize.

Diacetylacetone is also expected to form metal complexes as β-diketones. Moreover as it has three carbonyl groups in each molecule, it probably acts as both a bidentate and a tridentate ligand.

Sagara and his co-workers4) reported on Cu(II) and Ni(II) chelates containing bidentate or tridentate diacetylacetone. It has also been reported that trithiodiacetylacetone can be synthesized and isolated by the reaction of diacetylacetone and phosphorus pentasulfide.5) The present author has previously synthesized the Rh(III) and Pt(II) trithiodiacetylacetone complexes6) from the metal salts and the ligand. As an extension of this work, although the attempts at the synthesis of the cobalt complexes of trithiodiacetylacetone have not yet been successful, the monothiodiacetonates were obtained.

In this paper the synthesis and properties of Co(II) complexes of $C_7H_{10}SO_2$ as well as of $C_7H_{10}O_3$ will be described.

Experimental

Starting Materials. The cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and cobalt(II) bromide hexahydrate ($CoBr_2 \cdot 6H_2O$) of a G. R. Grade were used without further purification. The diacetylacetone (DAA) was synthesized from dehydroacetic acid by the method of Bethell and Maitland.7) The trithiodiacetylacetone (TTDAA) was obtained by the method of Arndt5) from DAA and phosphorus pentasulfide.

Syntheses of the Complexes. $Co(C_7H_{10}SO_2)_2X_2$: Powdered Co(II) halide hexahydrate and TTDAA were mixed (1 : 2 mole ratio) for 1 hr in an agate motor. During the procedure, the mixture turned green. The unreacted TTDAA was removed by washing with hot benzene. The crude product thus obtained was dissolved into chloroform, and the insoluble, unreacted cobalt halide was filtered off. The filtrate was concentrated using a rotary evaporator at about 50°C, and from the solution a green product was precipitated by adding

Table 1. Analysis and magnetic moments of complexes
(Analytical data are given in % and magnetic moments are given in B.M.)

		C	H	S	X	M	O*	B.M
$Co(II)(C_7H_{10}SO_2)_2Cl_2$	Calcd	37.68	4.53	14.37	15.89	13.20	14.33	4.46
	Found	37.80	4.10	15.30	15.00	13.40	14.41	
$Co(II)(C_7H_{10}O_3)_2Cl_2$	Calcd	40.60	4.88		17.12	14.23	23.17	4.77
	Found	41.55	4.62		17.56	14.50	23.53	
$Co(II)(C_7H_{10}SO_2)_2Br_2$	Calcd	31.42	3.77	11.98	29.86	11.01	11.96	4.77
	Found	32.00	3.21	11.90	30.90	10.90	11.31	
$Co(II)(C_7H_{10}O_3)_2Br_2$	Calcd	33.42	4.02		31.77	11.71	19.08	4.55
	Found	33.90	4.04		32.00	12.00	18.66	

* Obtained by substraction of the sum of the analyses of other elements from 100%

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1) A. E. Martell and M. Calvin, "The Chemistry of Metal Chelate Compounds," Prentice-Hall, INC. Engelewood Cliffs, N. J. (1952).

2) W. C. Fernelius, B. E. Bryant, *Inorg. Synthesis*, **5**, 105 (1957).

3) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966).

4) F. Sagara, H. Kobayashi and K. Ueno, This Bulletin, **41**, 266 (1968).

5) F. Arndt, P. Nacktwey and J. Pusch, *Ber.*, **58**, 1633 (1925).

6) A. Furuhashi, Y. Hayakawa and A. Ouchi, Symposium on Coordination Chemistry, Sendai, Sept. 1969.

7) J. R. Bethell and P. Maitland, *J. Chem. Soc.*, **1962**, 3751.

Table 2. Infrared spectra of complexes (Figures are given in cm^{-1}.)

$C_7H_{10}O_3$	$C_7H_8S_3$	$Co(C_7H_8O_3)_2Cl_2$	$Co(C_7H_8O_3)_2Br_2$	$Co(C_7H_8O_2S)_2Cl_2$	$Co(C_7H_8O_2S)_2Br_2$	Tentative assignments
1635 (br. v.s)	1640 (br. v.s)	1650 (v.s)	1650 (v.s)			
				1620 (s)	1625 (s)	C=C stretch
		1573 (m)	1573 (m)	1568 (w)	1568 (w)	
		1550	1550	1540 (m)	1540 (s)	
1540 (m)		1535 (s)	1535 (s)			
	1490 (s)	1488 (w)	1488 (w)			or C=O stretch
	1430 (w)	1450 (w)	1450 (w)	1440 (m)	1445 (m)	
		1418 (m)	1418 (m)		1400 (w)	CH_3 deform.
1395 (s)	1372 (s)	1380 (w)	1380 (w)	1375 (w)	1375 (w)	
1355 (s)		1350 (s)	1350 (s)		1350 (w)	
	1295 (s)			1285 (s)	1285 (s)	
1240 (s)	1250 (s)					
	1210 (s)	1202 (s)	1202 (s)			
1180 (s)		1170 (m)	1170 (m)	1170 (w)	1170 (w)	$C–CH_3$ stretch
1140 (s)						
	1120 (s)			1100 (s)	1102 (s)	
1035 (s)		1045 (m)	1045 (m)	1040 (w)	1030 (w)	
	1020 (w)			1007 (s)	1007 (s)	CH_3 rocking mode
978 (w)		960 (m)	961 (m)	950 (w)	950 (w)	CH deform.
945 (m)		909 (s)	909 (s)	940 (m)	942 (m)	(out of plane)
					910 (w)	
895 (s)		890 (m)	890 (m)	899 (v.w)	889 (w)	
		879 (m)	897 (m)	872 (w)		
	850 (v.s)			855 (s)	855 (s)	C–H out of plane bend
820 (v.s)						
750 (m)	740 (w)					
735 (s)	698 (s)			689 (m)	698 (m)	C=S stretch
	665 (m)					
		627 (m)	630 (m)			
	600 (m)					
555 (s)	595 (m)	555 (m)	557 (m)	570 (m)	570 (m)	$C–CH_3$ deform.
		525 (m.w)	528 (m.w)			
488 (s)	471 (m)	457 (v.w)	460 (v.w)	470 (v.w)	470 (w)	

v.s: very strong, s: strong, m: medium, w: weak, v.w: very weak, br: broad

an equivolume of petroleum ether.

$Co(C_7H_{10}O_3)_2X_2$: $Co(C_7H_{10}O_3)_2X_2$ was similarly synthesized using cobalt halide hexahydrate and DAA. The product was blue.

Instruments. The magnetic moments of the compounds were measured by Gouy's method at room temperature (25°C). The infrared spectra were obtained on a KBr disk sample by using a Model IR-G infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. The electronic spectra were obtained with a Shimadzu MPS-50-type automatic recording spectrophotometer. The NMR spectra were obtained with a Hitachi Perkin-Elmer Model-R-20 NMR spectrometer.

Results and Discussion

The analytical data and magnetic moments are summarized in Table 1.

The magnetic data show that these compounds have magnetic moments of 4.5—4.8 B.M. In the case of cobalt(II) complexes, the magnetic moment of the tetrahedral form is found mostly in the 4.4—4.7 B.M. range, that of the octahedral form in the 4.7—5.2 B.M. range and that of the square-planar form in the 2.4—2.8 B.M. range, because of the orbital angular momentum contribution. In view of these facts, it is reasonable to conclude that the compounds are tetrahedral.

The infrared spectra data of the compounds are summarized in Table 2.

As there are almost no differences between the spectra of chloro and bromo complexes, the chlorine or bromine can be said not to have any serious effect on the vibrational frequencies in the complexes. Two strong characteristic bands which seem to be ν (C=O) appear near the 1962—1650 cm^{-1} range.

It is rather difficult to assign the ν (C=S) bands of these compounds. Barraclough[8] has reported that the ν (C=S) bands appear near 660—750 cm^{-1}; he based the conclusion on the results of the coordination analyses as well as on the experimental data of the metal dithioacetylacetonato complexes. As the 698 cm^{-1} band of the $Co(C_7H_{10}SO_2)_2X_2$ seems to correspond to the 740, 698 and 665 cm^{-1} bands of $C_7H_8S_3$, it is probably the ν (C=S) band or at least one containing ν (C=S), although the intensity of the band of the metal complexes was not so strong as that of the bands of $C_7H_8S_3$. This fact seems to indicate that the $Co(C_7H_{10}SO_2)_2X_2$ has only one C=S bond, as is also shown by the analytical data. As the shift of the ν(C=S) band by the formation of the coordination bond with the central metal is not extensive, the bond between sulfur and the metal atom in the complex seems not to be strong.

The findings regarding the NMR spectra also support the above conclusion. The NMR spectra of TTDAA in $CDCl_3$ (standard : TMS) shows four peaks, at 7.45, 6.84, 2.60, and 2.18 ppm; the ratio of the areas of the peaks was 1 : 1 : 3 : 3. This can probably be explained by the fact that TTDAA has a five-membered ring containing as S–S bond and a free C=S bond, as is shown by Fig. 1.

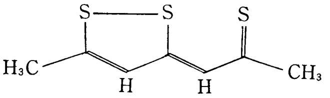

Fig. 1. Structure of TTDAA.

Therefore, both the methyl groups and the hydrogen atoms combined with 3rd and 5th carbon atoms are indifferent. The NMR spectra of both $Co(C_7H_{10}SO_2)_2X_2$ and $Co(C_7H_{10}O_3)_2X_2$ show only one peak, at about 2.58 ppm. Therefore, the two methyl groups of the ligand of the cobalt(II) compounds are symmetric; however, as these compounds are hardly soluble into $CDCl_3$, the peaks due to the hydrogen atoms bonding to the 3rd and 5th carbon atoms can not be deserved. The peaks of the latter hydrogen atoms were, however, found in the case of the DMF solution, 6.74 ppm for $Co(C_7H_{10}SO_2)_2X_2$ and 5.75 ppm for $Co(C_7H_{10}O_3)_2X_2$, although the effect of the solvent on the species may be a little different in this case. Consequently, in the case of $Co(C_7H_{10}O_3)_2X_2$, the central oxygen atoms of the ligand seem to bond with the cobalt atom, and in the case of $Co(C_7H_{10}SO_2)_2X_2$ the sulfur atom, which replaces the central oxygen atom of the $C_7H_{10}O_3$ ligand, is probably combined with the cobalt atom.

The electronic spectra of these compounds of a chloroform solution are summarized in Table 3.

The bands at about 38000—40000 cm^{-1} seem to be the π–π bands of the ligands. Trithiodiacetylacetonates of Cu(I) and Pt(II)[5] also show the band at 38000 cm^{-1}. Therefore, the band due to ligands moves to the lower wave number side as the number

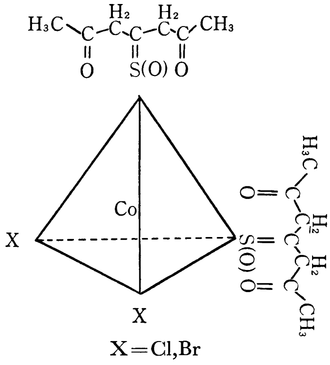

Fig. 2. Structure of Co(II) complex.

TABLE 3. ELECTRONIC SPECTRA OF COMPLEXES

(Figures are given in cm^{-1} for wave numbers and log ε for intensities (in parentheses).)

$C_7H_{10}O_3$	$C_7H_8S_3$	$Co(C_7H_{10}O_3)_2Cl_2$	$Co(C_7H_{10}O_3)_2Br_2$	$Co(C_7H_{10}SO_2)_2Cl_2$	$Co(C_7H_{10}SO_2)_2Br_2$
		40240 (4.10)			
39540 (3.62)			39920 (4.24)		
	38020 (4.82)			39370 (4.22)	39370 (4.31)
38020 (3.61)					
31250 (4.27)		30670 (sh) (2.49)	30670 (sh) (2.57)		
				28820 (4.60)	28820 (4.59)
	28090 (sh) (2.70)				
		26320 (sh) (1.99)	26600 (sh) (1.86)		
				24270 (sh) (3.21)	24270 (sh) (3.16)
		22220 (1.83)	22220 (1.00)		
	21140 (3.92)				

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[8] C. G. Barraclough, R. L. Martin and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).

of sulfur atoms in a ligand molecule increases.

The bands at about 22000—26000 cm^{-1} seem to be mixtures of d–d and d-π bands. Generally, tetrahedral cobalt(II) complexes have an intense band at about 15000 cm^{-1}. Although the solid compounds have an intense color, the solution of these compounds lost its intense color and turned pink rapidly. This is probably because the complexes decompose and change into octahedral complexes in such a dilute solution.

The results suggest that these compounds have a tetrahedral configuration and that the ligand works as a zero-valent monodentate in it. The structure shown in Fig. 2 is proposed for these compounds.

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