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Studies on the Sulfur-containing Chelating Agents. XXIII.[1] Some Investigations on the Quasiaromaticity of Cobalt(III) Thio-β-diketonates by the Spectroscopic Methods

Akira Yokoyama, Shosuke Kawanishi
and Hisashi Tanaka

Faculty of Pharmaceutical Sciences, Kyoto University[2]

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Infrared, electronic and nuclear magnetic resonance spectra of cobalt (III) thio-β-diketonates were studied in comparison with those of cobalt (III) β-diketonates. Quasiaromaticity was more strongly supported in thio-β-diketonates than in β-diketonates by mainly the following observations. In thio-β-diketonates, absorption bands of $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ wereobserved at lower wave number than in corresponding β-diketonates. Chemical shifts of the protons of methine and methyl groups were found in lower field in thio-β-diketonates than those of corresponding β-diketonates. In Co (III) thioacetylacetonate a singlet was observed as a signal of methyl groups in nonpolar solvents. In Co (III) thio-β-diketonates which contain phenyl group, deshielding effect and mesomeric effect of phenyl group were also discussed in nuclear magnetic resonance spectra.

In the previous paper,[1] we reported on the syntheses of thio-β-diketones and their metal chelates, and also on the bromination of the cobalt(III) chelates, and suggested that they have quasiaromaticity to some extent. Quasiaromaticity of metal β-diketonates has been discussed with various respects and many supporting results to their quasiaromaticity have been reported, whereas several questions still remain unsolved. Benzenoid resonance of the chelate ring in some β-diketonates has been proposed by Calvin,[3] for the explanation of their extreme stability, and in this connection, some of the metal β-diketonates have been investigated by various physico-chemical methods such as infrared[4] and nuclear magnetic resonance spectroscopy[5] and X-ray analysis.[6] In addition, electrophilic substitutions, such as halogenation, nitration and acylation were successful in some of the metal β-diketonates of octahedral types and quasiaromaticity was supported from the view point of the chemical reactivity.[7] However, some arguments are still being proposed against quasiaromaticity. Namely, Keller[8] and Holm[5a] pointed out that π-bonding can hardly be considered between metal and oxygen, because the oxygen does not have unoccupied orbital and back donation of the $3d$ electron of the metal to the oxygen can not be taken into consideration. On the contrary, when the

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ligand atom of β-diketone is replaced by sulfur, π-bonding between metal and sulfur can be considered, as proposed in various types of sulfur-coordinating complexes.[9] From this point of view, quasiaromaticity is considered to be more likely in the metal thio-β-diketonates than in β-diketonates. Recently several kinds of thio-β-diketones and their metal chelates were prepared,[10] but their properties have not been investigated in detail. As the quasiaromaticity was supported to some extent, in the cobalt(III) chelates of thio-β-diketones by the electrophilic substitution, namely the bromination, further discussions on the quasiaromaticity were attemped by the spectroscopic methods.

Experimental

Materials——Cobalt (III) chelates of 4-mercapto-3-penten-2-one (thioacetylacetone) (SAA), 3-mercapto-1-phenyl-2-buten-1-one (SAB), 4-mercapto-4-phenyl-3-buten-2-one (SBA) and 3-mercapto-1,3-diphenyl-2-propen-1-one (SBB) were prepared by the method reported previously.[1] Cobalt (III) chelates of β-diketones were prepared by the method reported in the literature.[11]

Electronic Spectra——The spectra were measured on a Hitachi recording spectrophotometer model EPS-2.

Nuclear Magnetic Resonance Spectra——NMR spectra in $CDCl_3$ were measured, by Varian A-60 spectrometer at 60 Mc. with tetramethylsilane as internal standard. The concentration of the solution was 5×10^{-2} mole/liter.

Infrared Spectra——The spectra were measured as potassium bromide disks in the range 4000—400 cm^{-1} on Koken DS 301 spectrophotometer.

Results and Discussions

Infrared and Electronic Spectra

Wave numbers and the possible assignments of the main absorption bands in infrared spectra of the Co (III) chelates of thio-β-diketones and those of β-diketones are listed in Table I. The assignments in thio-β-diketonates were made by reference to the recent assignments in β-diketonates.[12] The quasiaromaticity of the cobalt (III) β-diketonate has been explained by the lower shift of the wave numbers of the absorption bands of $\nu(C \!=\!\!= O)$ and $\nu(C \!=\!\!= C)$. In the case of Co (III) thio-β-diketonate, the absorption band of $\nu(C \!=\!\!= C)$ was ob-

Table I. Infrared Spectral Bands of Cobalt (III) Chelates of Thio-β-diketones and β-Diketones in KBr Disks

Ligand	Bands (cm^{-1}) $\nu(C \!=\!\!= O)$	$\nu(C \!=\!\!= C)$	Ligand	Bands (cm^{-1}) $\nu(C \!=\!\!= O)$	$\nu(C \!=\!\!= C)$
SAA	1573	1468	AA	1578	1527
SAB	1550	1460	AB	1555	1515
SBA	1565	1475			
SBB	1543	1473	BB	1535	1520

AA: acetylacetone AB: benzoylacetone BB: dibenzoylmethane

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9) S.E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

10) *a*) S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer and V.A. Pickles, *Australian J. Chem.*, **18**, 673 (1965); *b*) *Idem, ibid.*, **20**, 1065 (1967); *c*) E. Uhlemann, G. Klose and H. Müller, *Z. Naturforsch*, **19b**, 962 (1964); *d*) E. Uhlemann and Ph. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966); *e*) *Idem*, *Z. Anorg. Allg. Chem.*, **356**, 71 (1967).

11) *a*) H.F. Bauer and W.C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960); *b*) R.C. Fay and T.S. Piper, *ibid.*, **84**, 2303 (1962).

12) *a*) S. Pinchas, B.L. Silver and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967); *b*) G.T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967); *c*) H. Musso and H. Junge, *Tetrahedron Letters*, 33, 4003 (1966).

served at lower wave number than in the case of β-diketonate. These observations suggest that in thio-β-diketonates, the delocalization of the π-electrons are more positively supported than in the case of β-diketonates.

In the transition metal chelates of acetylacetone,[11b,13] absorption bands caused by the π–π^* of the ligands and those caused by the charge transfer were clearly observed in the visible and ultraviolet region and also the absorption caused by the $3d$ electron of metal was observed. In comparison of the electronic spectra of cobalt (III) thio-β-diketonate with those of cobalt (III) β-diketonate, in the former, the absorption maxima were observed in the region of longer wave length, and molar absorptivity of d–d^* transition band is greater than in the latter, as seen in Table II.

Table II. Electronic Spectral Bands of Cobalt (III) Chelates of Thio-β-diketones and β-Diketones in Chloroform Solution

Ligand	d—d^*[d] mμ	(ε)[c]	Charge transfer[d] mμ	(ε)[c]	π—π^*[d] mμ	(ε)[c]
SAA	600	(380)	388	(8100)	285	(30600)
SAB	602	(580)	410	(14600)	287	(50600)
SBA	602	(510)	386	(9600)	302	(62600)
SBB	605	(750)	410	(15500)	310	(80000)
AA[a]	592	(129)	325	(7940)	257	(34700)
AB[b]	598	(154)	355	(13400)	262	(53300)
BB	600	(215)	383	(19900)	283	(90100)

a) lit.[13] *b*) lit.[11b] *c*) molar absorptivity *d*) provisional assignment
AA: acetylacetone AB: benzoylacetone BB: dibenzoylmethane

However, it is difficult to discuss the quasiaromaticity from the these data of the electronic spectra.

Nuclear Magnetic Resonance Spectra

Holm[5a] proposed the following argument against the benzenoid resonance of the chelate ring of the metal acetylacetonate from the investigation of the nuclear magnetic resonance spectra. The chemical shifts of the proton in methine and methyl group were observed in the region ranging from 4.50 ppm to 4.75 ppm and from 7.87 ppm to 8.10 ppm, respectively in metal acetylacetonates, whereas the ligand acetylacetone itself showed the chemical shift at 4.6 ppm and 8.0 ppm, respectively. The above-mentioned fact that the chemical shift was found to be almost similar regardless of the chelate formation gives rise to the argument against the existence of benzenoid resonance in the metal chelates.

In Table III, the results of the measurements of nuclear magnetic resonance spectra of cobalt (III) β-diketonates and cobalt (III) thio-β-diketonates are summarized. As shown in Table III, the chemical shifts of the protons of the methine groups were found to be lower in thio-β-diketonates than those of the corresponding β-diketonates. The values observed in thio-β-diketonates are far lower than the normal value of the olefinic proton and in the range of those of the hetero aromatic rings, such as pyridine, thiophene, furan and pyrrole. In addition, values of the chemical shifts of methyl proton are rather close to that of toluene than that of ordinary aliphatic compounds. In the case of cobalt (III) thioacetylacetonate, a singlet was observed in nonpolar solvent as a signal of the methyl group, whereas in the case of nickel, zinc and palladium thioacetylacetonate doublet was observed. This fact may suggest the possibility of the existence of the ring current in the chelate ring of the cobalt thioacetylacetonate. As reported before,[1] in the case of tris-(γ-bromo-thioacetylacetonato)-

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13) D.W. Barum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

cobalt (III), the signal of methyl group splits into doublet, on account of considerable localization of π-electrons, caused by the introducing electron-negative bromine atom. Abovementioned observations in nuclear magnetic resonance spectra are considered to be very interesting in connection with the quasiaromaticity of the chelate ring and the explanation of the facts are still under investigation. Although these data on nuclear magnetic resonance spectra seem to support the quasiaromaticity, the fact that the value of the chemical shift of methine proton of the ligand is close to that of the cobalt chelate will still propose a question. However, if the ligand itself is considered to have the quasiaromaticity to some extent[14] this fact may be explained.

TABLE III. Chemical Shifts of Cobalt (III) Chelates of Thio-β-diketones and β-Diketones in $CDCl_3$

Ligand	τ-Values		Ligand	τ-Values	
	=CH–	$-CH_3$		=CH–	$-CH_3$
SAA	3.62	7.76	AA	4.46	7.82
SAB	2.91	7.60	AB	3.76	7.62
SBA	3.30	7.60			
SBB	2.65		BB	3.08	

AA: acetylacetone AB: benzoylacetone BB: dibenzoylmethane

Influence of Phenyl Group

Among the cobalt (III) thio-β-diketonates of four different ligands, considerable differences were observed between thioacetylacetonate and other chelates involving phenyl group, as in the case of β-diketonates. Therefore, the influence of phenyl group towards the quasiaromaticity was discussed by the infrared and nuclear magnetic resonance spectra. In the case of the chelates involving phenyl group the signal of methine proton was observed in lower field than that of thioacetylacetonate. As to the reasons of this observation, two factors, namely the deshielding effect and mesomeric effect of the phenyl group, can be taken into account. Provided that the phenyl group and chelate ring are present on the same plane, the extent of the shift toward lower field caused by the deshielding effect of phenyl group can be calculated by the use of Johnson-Bovey's diagram[15] as 0.45 ppm, as the distances between the proton of the chelate ring and the center of phenyl group can be estimated by use of X-ray results[16] as 3.90 Å, which corresponds to about 65% of the total shift of about 0.7 ppm as shown in Table III. Remaining about 35% is considered to be attributed to the mesomeric effect of phenyl group. In order to discuss on the mesomeric effect, the relationship between the wave number of ν(C=O) and τ values of methine protons is presented in Fig. 1. The linearity seen in Fig. 1 shows the existence of mesomeric effect.

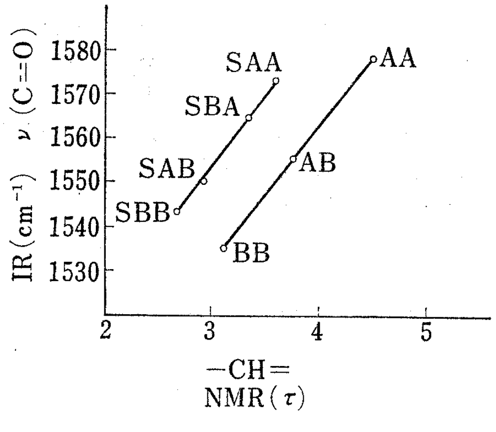

Fig. 1. Relationship between ν (C=O) and τ (–CH=) in Cobalt Chelates of Thio-β-diketones and β-Diketones

AA: acetylacetone AB: benzoylacetone
BB: dibenzoylmethane

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Judging from above discussions, it would be possibly concluded that the quasiaromaticity can be more strongly supported in thio-β-diketonate than in β-diketonate.

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