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Chemical and Spectroscopic Studies in Metal β-Diketonates. IV. Simpler Preparations of Metal 1,3-Diketonates and their Thiocyanation

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Tris(3-thiocyanato-2,4-pentanediono) Fe^{III}, bis(3-thiocyanato-2,4-pentanediono) Pd^{II}, tris(2-thiocyanato-1-phenyl-1,3-butanediono) Cr^{III}, tris(2-thiocyanato-1,3-diphenyl-1,3-propanediono) Cr^{III}, tris(2-thiocyanato-1-phenyl-1,3-butanediono) Co^{III} and tris(2-thiocyanato-1,3-diphenyl-1,3-propanediono) Co^{III} have been prepared by the thiocyanation of corresponding metal 1,3-diketonates with thiocyanogen. Possible mechanism of thiocyanation has been outlined. Rates of reactions and relative yields have been discussed in terms of principal steric and electronic effects of the substituents in the chelate rings. Dibenzoylmethane has been found to replace acetylacetone from the labile metal acetylacetonates providing a method for the preparation of metal dibenzoylmethanates. Infrared and electronic spectral data have been recorded and are discussed.

Introduction

During a detailed general study of reactions of metal β-diketonates we have sought to demonstrate the aromatic nature of these chelate rings by comparison of the properties of such complexes with those of known aromatics. Substitution of halogens and nitro group at the central carbon atom of metal acetylacetonate, metal benzoylacetonate and metal dibenzoylmethanate chelate rings has been successfully carried out under electrophilic substitution reaction conditions in our[1-4] and other[5-7] laboratories. Results of our chemical and spectroscopic study on the thiocyanation reaction by thiocyanogen on the same chelate rings are reported in the present paper. Tris(3-thiocyanato-2,4-pentanediono) Fe^{III}, bis(3-thiocyanato-2,4-pentanediono) Pd^{II}, tris(2-thiocyanato-1-phenyl-1,3-butanediono) Cr^{III}, tris(2-thiocyanato-1,3-diphenyl-1,3-propanediono) Cr^{III}, tris(2-thiocyanato-1-phenyl-1,3-butanediono) Co^{III}, and tris-(2-thiocyanato-1,3-diphenyl-1,3-propanediono) Co^{III} have been prepared by thiocyanation of appropriate chelates either by lead thiocyanate and bromine in 1,2-dichloroethane or potassium thiocyanate and bromine in methanol.

Experimental Section

Melting points were determined on a Mel-Temp. melting point apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 137-B infracord spectrophotometer (4000-670 cm^{-1} region) in KBr or Nujol mulls. Ultraviolet and visible spectra were obtained using Beckman DB or Cary-14 recording spectrophotometer in chloroform (10^{-5}–10^{-2} *M*).

Preparation of 1,3-diketonates. Metal β-diketonates were prepared by the known[8,9] or by simpler methods which in general involved (I) addition of calculated amount of β-diketone to an excess of the metal oxide in appropriate redistilled solvent, the reaction being accelerated by heating and refluxing.

(II) Refluxing of a suspension of metal chloride and ligand in stoichiometric amounts in suitable solvents for long time (40-50 hours).

(III) Ligand exchange reactions in suitable solvents.

Tris(2,4-pentanediono) Sc^{III} i.e. Sc(acac)$_3$. Was prepared according to procedure (I). Acetylacetone, 3.0 ml (0.03 mole) and an excess of scandium oxide (0.015 mole) taken in 30 ml of redistilled dry ether were refluxed for 3 hours. The hot yellow solution was filtered which gave light yellow, needle shaped crystals on slow evaporation. Recrystallization from benzene-ether gave analytical sample, m.p. 187°, in 55% yield of the theoretical.

Anal. Calcd. for $C_{15}H_{21}ScO_6$: C, 52.63; H, 6.14; Sc, 13.15. Found C, 53.22; H, 5.81; Sc, 13.80.

Tris(1-phenyl-1,3-butanediono) Cr^{III} i.e. Cr(BA)$_3$. Was prepared by procedure (I) (benzoylacetone, 0.05 mole and an excess of Cr_2O_3 (0.015 mole) in chloroform) and procedure (II) (benzoylacetone, 0.03 mole and $CrCl_3 . 6H_2O$, 0.01 mole in chloroform or cyclohexane). The suspension of reaction mixture in both cases was refluxed for 50 hours. It was filtered hot and diluted with ethanol. Reddish-brown precipitate of Cr(BA)$_3$ thus produced was filtered off and washed with ether. An analytical sample, m.p. 239-40°, was obtained in 60 and 50% yield respectively by four recrystallizations from benzene-heptane.

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(1) P. R. Singh and R. Sahai, *Aust. J. Chem.*, *20*, 639 (1967).
(2) P. R. Singh and R. Sahai, unpublished result.
(3) P. R. Singh and R. Sahai, *Aust. J. Chem.*, *20*, 649 (1967).
(4) P. R. Singh and R. Sahai, under publication.
(5) J. P. Collman, *Adv. Chem. Ser.*, *37*, 78 (1963).
(6) J. P. Collman, *Angew. Chem. Int. Edn.*, *4*, 132 (1965).
(7) J. P. Collman, "Transition metal Chemistry", 2, 1 (1966).
(8) L. E. Marchi, "Inorganic Syntheses", 2, 10 (1947).
(9) W. C. Fernelius and B. E. Bryant, "Inorganic Syntheses", 5, 105 (1957).

Anal. Calcd. for $C_{30}H_{27}CrO_6$: C, 67.28; H, 5.04; Cr, 9.72;. Found: C, 66.41; H, 4.82; Cr, 10.25.

Tris(1,3-diphenyl-1,3-propanediono) Cr^{III} i.e. *Cr(DBM)*$_3$. Was prepared according to procedures (I) and (III). The procedure (I) was essentially the same as in the case of Cr(BA)$_3$ except that 0.03 mole of DBM instead of BA was used. In procedure (III) Cr(acac)$_3$, (0.004 mole) and DBM, (0.012 mole) were dissolved in 20 ml dimethylformamide and refluxed for 50 hours. The clear red brown solution was poured over ice-cold water. The green precipitate that separated was filtered, washed with water and recrystallized from benzene-heptane. The yield of brown crystals was 80% of the theoretical. An analytical sample, m.p. 318-19°C, was obtained by five recrystallizations from benzene-heptane.

Anal. Calcd. for $C_{45}H_{33}CrO_6$: C, 74.89; H, 4.57; Cr, 7.21. Found: C, 75.78; H, 4.23; Cr, 7.50.

Tris(1,3-diphenyl-1,3propanediono) Fe^{III} i.e. *Fe(DBM)*$_3$. Was prepared according to procedure (III). Fe(acac)$_3$, 0.706 gm (0.002 mole) was dissolved in 20 ml hot ethanol and a solution of DBM, 1.342 gm (0.006 mole) in 10 ml hot ethanol was added to it slowly with constant stirring. On keeping the reaction mixture for five minutes shining reddish-brown crystals separated which were filtered under suction and washed with cold ethanol. Yield 92% of the theoretical. An analytical sample, m.p. 261-62°, was obtained by recrystallization from chloroform.

Anal. Calcd. for $C_{45}H_{33}FeO_6$: C, 74.48; H, 4.55; Fe, 7.70. Found: C, 73.25; H, 4.31; Fe, 8.01.

Bis(1,3-diphenyl-1,3-propanediono) Cu^{II} i.e. *Cu(DBM)*$_2$. Was prepared according to procedure (III). Cu(acac)$_2$, 1.04 gm (0.004 mole) was dissolved in 30 ml hot chloroform and a solution of DBM, 1.80 gm (0.008 mole) in 10 ml hot chloroform was added to it slowly with constant stirring. Dirty green shining crystals that separated after keeping the reaction mixture for five minutes, were filtered under suction and washed with cold chloroform. Yield 85% of the theoretical. An analytical sample, m.p. 297-300°, was obtained by recrystallization from toluene.

Anal. Calcd. for $C_{30}H_{22}CuO_4$: C, 70.65; H, 4.29; Cu, 12.46. Found: C, 71.11; H, 4.56; Cu, 12.58.

Tris(1-phenyl-1,3-butanediono) Al^{III} i.e. *Al(BA)*$_3$. Was prepared by procedure (I). The details were essentially the same as in the case of Sc(acac)$_3$ except that 0.03 mole of benzoylacetone and 0.015 mole Al_2O_3 was used instead of acetylacetone and Sc_2O_3 respectively. Recrystallization from benzene-ether gave analytical sample, m.p. 242-43°, in 50% yield of the theoretical.

Anal. Calcd. for $C_{30}H_{27}AlO_6$: C, 70.58; H, 5.29; Al, 5.29. Found: C, 71.32; H, 4.82; Al, 5.48.

Tris(1,3-diphenyl-1,3propanediono) Al^{III} i.e. *Al(DMB)*$_3$. Was prepared according to procedure (III) as in the case of Fe(DBM)$_3$ except that 0.002 mole of Al(acac)$_3$ instead of Fe(acac)$_3$ was used. Recrystallization from benzene-ether gave analytical sample, m.p. 270°, in 85% yield of the theoretical.

Anal. Calcd. for $C_{45}H_{33}AlO_6$: C, 77.58; H, 4.74; Al, 3.87. Found: C, 76 40; H, 5.12; Al, 3.95.

Attempted ligand exchange reaction on Co^{III} acetylacetonate by dibenzoylmethane on the same lines as in the case of Cr(acac)$_3$, was unsuccessful. Only starting material *i.e.* Co(acac)$_3$, m.p. 214°, was recovered.

Thiocyanation. The thiocyanation of Al^{III}, Cr^{III}, Co^{III}, and Cu^{II} acetylacetonates was done as reported in the literature.[10-12] For spectroscopic studies products were purified by several recrystallizations from suitable solvents. The introduction of thiocyanato group at the central carbon atom of other β-diketonate rings was effected by one or more of the following methods:

(I) Thiocyanogen in 1,2-dichloroethane was prepared by dropwise addition of 5 ml 1,2-dichloroethane solution of bromine, 0.5 gm (0.003 mole) to a vigorously stirred suspension of anhydrous lead thiocyanate, 1.10 gm (0.003 mole) in the same solvent (10 ml) cooled to −15 to −20°C. The red bromine colour was allowed to disappear before each successive addition of bromine. The mixture of thiocyanogen and lead bromide was stirred for 5 minutes after the addition of bromine was completed. The solid lead bromide was allowed to settle and the colourless supernatant liquid containing thiocyanogen was filtered into a stirred solution of metal β-diketonate (0.001 mole) in 15 ml of 1,2-dichloroethane cooled to −15 to −30°C. The mixture was stirred for 2-3 hours at −15 to −30°C and then allowed to sit at room temperature for an additional hour. The desired product was isolated from reaction mixture by washing the mixture twice with water containing sodium acetate, then thoroughly with water, drying organic phase over calcium chloride, filtering and (a) evaporating the solvent to dryness (for inert chelates); (b) evaporating to dryness in vacuum (for labile chelates). The product thus obtained in both cases as powder was recrystallised from suitable solvent for further purification.

(II) A solution of metal β-diketonate (0.012 mole) in methanol (40 ml) was added to a solution of potassium thiocyanate (0.084 mole) in methanol (50 ml). A solution of bromine (0.042 mole) in methanol (5 ml) (previously saturated with potassium bromide) was then added slowly with stirring, the former solution being maintained at −15 to −25°C. After stirring vigorously for 30 minutes the mixture was poured over ice-cold water (150 ml) buffered with sodium acetate. The residue was filtered, dried and recrystallized from a suitable solvent to give the desired pure product. This method was useful for thiocyanation of only those chelates which are soluble in methanol.

Tris(3-thiocyanato-2,4-pentanediono) Fe^{III} i.e. *Fe(NCS–acac)*$_3$. Was prepared according to methods (I) and (II); recrystallization from ethanol gave red crystals in 70 and 65% yield respectively, m.p. 167-68°.

Anal. Calcd for $C_{18}H_{18}N_3S_3FeO_6$: C, 41.21; H, 3.43; N, 8.01; Fe, 10.68. Found: C, 42.01; H, 3.12; N, 8.90; Fe, 10.78.

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(10) R. W. Kluiber, *J. Am. Chem. Soc.*, *83*, 3030 (1961).

(11) J. P. Collman, R. L. Marshall, W. L. Young III, and C. T. Sears Jr., *J. Org. Chem.*, *28*, 1449 (1963).

(12) D. N. Sen and N. Thankarajan, *Ind. J. Chem.*, *4*, 94 (1966).

Tris(2-thiocyanato-1-phenyl-1,3-butanediono) Cr^{III} i.e. *Cr(NCS–BA)*$_3$. Was prepared by method (I); recrystallization from chloroform-ethanol gave reddish-brown crystals in 80% yield; m.p. 172-73°.

Anal. Calcd. for $C_{33}H_{24}H_3S_3O_6Cr$: C, 56.09; H, 3.40; N, 5.94; Cr, 7.34. Found: C, 57.23; H, 3.74; N. 5.42; Cr, 7.52.

Tris(2-thiocyanato-1,3-diphenyl-1,3-propanediono) Cr^{III} i.e. *Cr(NCS–DBM)*$_3$. Was prepared according to method (I); recrystallization from chloroform-ethanol gave reddish-brown crystals, m.p. 230-31°, in 65% yield.

Anal. Calcd. for $C_{48}H_{30}O_6N_3S_3Cr$: C, 64.57; H, 3.36; N, 4.70; Cr, 5.82. Found: C, 65.68; H, 3.65; N, 5.10; Cr, 5.96.

Tris(2-thiocyanato-1-phenyl-1,3-butanediono) Co^{III} i.e. *Co(NCS–BA)*$_3$. Was prepared by method (I); recrystallization from chloroform-ethanol gave green crystals, m.p. 135-36°, in 75% yield of the theoretical.

Anal. Calcd. for $C_{33}H_{24}N_3S_3O_6Co$: C, 55.54; H, 3.36; N, 5.89; Co, 8.27. Found: C, 56.72; H, 3.84; N, 6.12; Co, 8.50.

Tris(2-thiocyanato-1,3-diphenyl-1,3-propanediono) Co^{III} i.e. *Co(NCS–DBM)*$_3$. Was prepared according to method (I); recrystallization from chloroform-ethanol gave green crystals m.p. 194-95° in 62% yield of the theoretical.

Anal. Calcd. for $C_{48}H_{30}N_3S_3O_6Co$: C, 64.07; H, 3.36; N, 4.67; Co, 6.56. Found: C, 63.16; H, 3.89; N, 5.23; Co, 6.81.

Bis(3-thiocyanato-2,4-pentanediono) Pd^{II} i.e. *Pd-(NCS–acac)*$_2$. Was prepared as in method (I) and recrystallized from chloroform to give yellow needle shaped crystals, m.p. 195-96° (dec.); yield 65% of the theoretical.

Anal. Calcd. for $C_{12}H_{12}N_2S_2O_4Pd$: C, 34.45; H, 2.86; N, 6.70; Pd, 25.35. Found: C, 33.39; H, 3.01; N, 6.25; Pd, 25.62.

Results and Discussion

In the preparation of metal 1,3-diketonates by ligand transfer reactions it is observed that dibenzoylmethane replaces acetylacetone from the complexes of the latter. The ease of this ligand transfer is determined by the labile nature of the acetylacetonates;[13,14] in the case of Co(acac)$_3$ which is known to be least labile, ligand transfer with DBM does not take place under the conditions employed. Benzoylacetone does not replace acetylacetone in any of the cases studied.

It is noticeable that the yields of the thiocyanato complexes in reactions of thiocyanogen (thiocyanation reagent) with metal 1,3-diketonates fall as the methyl groups of acetylacetonates are successively replaced by phenyl groups. In general reactions of acetylacetonates are faster than their analogues carrying phenyl substituents. Although, the phenyl groups tend to increase the electron density at the central carbon atom of the chelate ring (the reaction site) as a result of the mesomeric electron release by the phenyl group to the chelate ring, enhancing the reactivity of the chelate ring electronically, the steric effects of the coplanar phenyl group at the ortho position to the reaction site appears to be more important in these reactions.

The reaction time of 2-3 hours requirred for thiocyanation by (SCN)$_2$ of β-diketonates in 1,2-dichloroethane is reduced to about 30 minutes when more polar solvent-methanol is used. This trend is similar to that found by us during halogenation of metal acetylacetonates.[1] It has also been reported[15] that the reactivity of thiocyanogen in aromatic substitution is enhanced by Friedel-Crafts catalysts. In view of the above we suggest that during the reaction, polarization

Table I. Infrared absorption frequencies (cm^{-1}) of metal β-diketonates

Sc(acac)$_3$	Cr(BA)$_3$	Cr(DBM)$_3$	Fe(DBM)$_3$	Co(BA)$_3$	Co(DBM)$_3$	Al(BA)$_3$	Al(DBM)$_3$	Cu(DBM)$_2$	Possible Assignments
3000 vw	3030 vw	3030 vw	3030 vw	3030 vw	3030 vw	3030 vw	3030 vw	3030 vw	=C—H str.
1570 s	1545 s	1545 sh	1540 s	1545 s	1540 s	1550 s	1545 s	1550 s	$C\overset{\cdots}{-}O$ str.
1521 s	1520 s	1525 s	1520 s	1520 s	1520 s	1520 s	1520 s	1515 s	$C\overset{\cdots}{-}C$ str. coupled with C—H in plane bend. mode.
1415 w	1410 sh	—	—	1415 sh	—	1410 w	—	—	CH$_3$ deg. def.
1375 s	1367 s	1373 s	1385 s	1382 s	1380 s	1370 s	1365 s	1400 s	$C\overset{\cdots}{-}O$ str. coupled with C—H bend. mode.
1363 sh [a]	1355 sh	—	—	1360 m	—	1350 w	—	—	—
1265 m	1285 m	1305 m	1312 m	1295 m	1315 m	1300 m	1318 m	1298 m	$C\overset{\cdots}{-}C$ str. coupled with C—R str. mode.
1190 m	1205 m	1225 m	1225 m	1210 m	1225 m	1205 m	1225 m	1225 m	C—H in plane bend.
1020 m	1025 m	—	—	1025 m	—	1025 m	—	—	CH$_3$ rocking.
1010 m									
935 m	—	945 m	945 m	—	955 m	—	950 m	945 m	C—R sym. str. + other modes.
900 vw	—	930 w	925 w	—	930 w	—	930 w	932 w	C—R antisym. str.
—	855 m	—	—	855 m	—	855	—	—	—
810 m									
780 m	772 s	760 m	760 m	770 m	755 m	775 m	760 m	745 m	C—H out of plane bend.
685 w	690 m	690 m	690 m	690 m	690 m	695 m	685 m	680 m	M—O str. + ring def. + C—R str.

[a] CH$_3$ sym. def. s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

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(13) L. Wolf, E. Butter, and H. Weinelt, *Z. anorg. u. allgem. Chem.*, 306, 87 (1960).

(14) G. Schwarzenbach, *Angew. Chem.*, *70*, 451 (1958).

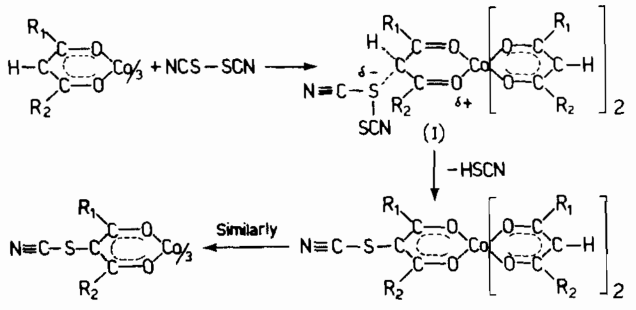
(15) E. Söderbäck, *Acta Chem. Scand.*, *8*, 1851 (1954).

Table II. Infrared absorption frequencies (cm^{-1}) of thiocyanated metal β-diketonates

Compound	Possible Assignments												
	C≡N str.	C$\overset{\cdots}{-}$O str.	C$\overset{\cdots}{-}$C str.	—	CH$_3$ deg. def.	—	—	C$\overset{\cdots}{-}$C str. + C–R str.	—	CH$_3$ rock.	—	C–S str. + Ring def. and M–O str.	M–O str. + Ring def. and C–R str.
$(C_6H_6NSO_2)_3Al$	2155 sp	1590 s	1530 sh	1460 sh	1420 s	1370 s	1340 s	1285 vw	1075 s	1025 s	935 m	715 s	—
$(C_6H_6NSO_2)_3Cr$	2160 sp	1580 s	1515 m	1450 sh	1415 m	1370 s	1340 s	1280 w	1070 s	1030 s	930 m	715 s	690 w
$(C_{11}H_8NSO_2)_3Cr$	2160 sp	1540 s	1500 m	1450 sh	1425 m	1365 m	1340 s	1290 vw	1050 m	1025 m	920 w	715 m	690 m
$(C_{16}H_{10}NSO_2)_3Cr$	2085 sp	1535 s	1510 sh	1440 sh	—	—	1335 s	1300 m	1070 w	—	930 w	710 m	700 m
$(C_6H_6NSO_2)_3Co$	2155 sp	1560 s	1500 sh	1450 m	1395 m	1355 s	1330 s	1270 vw	1060 s	1025 s	920 m	720 s	690 m
$(C_{11}H_8NSO_2)_3Co$	2160 sp	1540 s	1515 sh	1450 sh	1425 m	1355 m	1330 s	1295 vw	1050 m	1025 m	925 w	710 m	695 m
$(C_{16}H_{10}NSO_2)_3Co$	2165 sp	1535 s	1500 sh	1440 sh	—	—	1330 s	1315 w	1060 w	—	920 vw	720 m	702 m
$(C_6H_6NSO_2)_3Fe$	2165 sp	1570 s	1520 m	1450 sh	1420 m	1370 s	1335 s	1280 w	1060 m	1025 m	925 m	715 m	690 m
$(C_6H_6NSO_2)_2Cu$	2160 sp	1575 s	1520 m	1460 vw	1410 m	1370 s	1345 s	1270 vw	1070 m	1020 m	930 w	720 m	695 w
$(C_6H_6NSO_2)_2Pd$	2160 sp	1550 s	1510 sh	1455 w	1400 w	1360 s	1345 s	1270 vw	1060 m	1020 m	930 m	725 m	695 m

sp, sharp; s, strong; m, medium; w, weak: vw, very weak; sh. shoulder.

of S–S bond in thiocyanogen may occur. By analogy with the mechanism postulated for aromatic substitution effected by molecular halogens,[16] nuclear thiocyanation by $(SCN)_2$ may be considered to involve polarization of S–S bond, most probably aided by associated polar molecules of the solvent (or Friedel-Crafts catalysts) in a transition state or activated complex as (I). Most probable mechanism of thiocyanation by $(SCN)_2$ may thus be outlined taking a Co^{III} β-diketonate as example:



Infrared Spectra. The main I.R. absorption frequencies of the metal 1,3-diketonates and their possible assignments are recorded in Table I. We consider the frequencies in the region 1595-1590 cm^{-1} assigned to C=C str. in benzoylacetonates and dibenzoylmethanates of Cu^{II} and Ni^{II} by Nakamoto *et al.*[17] as being due to phenyl ring and not due to chelate ring. Our assignments are based on the results of thiocyanation and nitration studies on acetylacetonates, benzoylacetonates and dibenzoylmethanates of different metals; while C=C bond is significantly weakend due to substitution of a nitro[4] or a thiocyanato group at the central carbon atom of the chelate ring, the C=O bond is not so much weakend. These assignments are also in accord with the results of Nakamoto and Behnke[18] which have been quite helpful. A very weak absorption band in the region 3030-3000 cm^{-1} assigned to =C–H str. overlaps in most cases with the phenyl absorption band of comparable intensity. It is evident that on replacement of one of the methyl groups in acetylacetonates by a phenyl group the carbon-oxygen bonds are significantly weakend. Introduction of second phenyl group in place of methyl group, however, does not further weaken these bonds much. C=O str. frequency due to replacement of methyl groups by phenyl groups is not quite regular. A similar trend in the C=O str. and C=C str. frequency is apparent from

Table III. Electronic absorption spectra of metal β-diketonates and their thiocyanated derivatives

Metal β-diketonates	λmax (mμ); log ϵ	Thiocyanated derivatives	λmax (mμ); log ϵ
$(C_5H_7O_2)_3Al$	288; 4.582	$(C_6H_6NSO_2)_3Al$	283; 4.475
$(C_{10}H_9O_2)_3Al$	250; 3.95 320; 4.30	—	—
$(C_{15}H_{11}O_2)_3Al$	258; 4.16 348; 4.65	—	—
$(C_5H_7O_2)_3Sc$	297; 4.45	—	—
$(C_5H_7O_2)_3Cr$	270; 4.021 335; 4.23 560; 1.86	$(C_6H_6NSO_2)_3Cr$	273; 4.477 332; 3.903 558; 1.87
$(C_{10}H_9O_2)_3Cr$	274; 4.281 359; 4.364 564; 1.94	$(C_{11}H_8NSO_2)_3Cr$	270; 4.272 345; 4.40 561; 2.113
$(C_{15}H_{11}Q_2)_3Cr$	360; 4.50 385; 4.52 568; 2.07	$(C_{16}H_{10}NSO_2)_3Cr$	353; 4.45 370; 4.49 566; 2.10
$(C_5H_7O_2)_3Fe$	274; 4.723 353; 3.522 437; 3.515	$(C_6H_6NSO_2)Fe$	272; 4.50 352; 3.75 428; 3.53
$(C_{15}H_{11}O_2)_3Fe$	248; 4.342 312; 4.65 383; 3.86 460; 3.75	—	—
$(C_5H_7O_2)_3Co$	258; 4.544 325; 3.90 593; 2.105	$(C_6H_6NSO_2)_3Co$	261; 4.420 (320); 3.815 591; 1.95
$(C_{10}H_9O_2)_3Co$	265; 4.74 355; 4.05 598; 2.18	$(C_{11}H_8NSO_2)_3Co$	270; 4.591 (355); 3.96 590; 2.32
$(C_{15}H_{11}O_2)_3Co$	288; 4.602 380; 4.10 603; 2.34	$(C_{16}H_{10}NSO_2)_3Co$	290; 4.61 370; 4.02 592; 2.88
$(C_5H_7O_2)_2Cu$	246; 4.20 296; 4.415 560; 1.50 670; 1.56	$(C_6H_6NSO_2)_2Cu$	245; 4.14 294; 4.45 645; 1.77
$(C_{15}H_{11}O_2)_2Cu$ [a]	260; 3.28 350; 4.58 650; 1.88 (685); 1.86	—	—
$(C_5H_7O_2)_2Pd$	330; 4.38	$(C_6H_6NSO_2)_2Pd$	327; 4.05

[a] Spectra taken in dioxane. Shoulder bands are given in parentheses.

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(16) P. B. D. Dela Mare and J. H. Ridd, "Aromatic substitution. Nitration and Halogenation", Butterworths, London (1959).

(17) K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Phys. Chem.*, 66, 346 (1962).

(18) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 6, 433, 440 (1967).

(19) R. D. Hancock and D. A. Thornton, *Inorg. Nucl. Chem. Letters*, 3, 423 (1967).

the data obtained by Hancock and Thornton.[19] Neglecting the weak negative inductive effect of the phenyl group and looking at the principal electronic effects in the mesomeric interactions of the phenyl ring with the quasi-aromatic metal chelate ring one would also expect C–H in plane bending absorption to shift to higher frequencies due to phenyl substitution. This has actually been found.

The principal I.R. absorption bands for thiocyanated metal 1,3-diketonates and their possible assignments are given in Table II. Disappearance on thiocyanation of the C–H in plane bending vibration in the region 1225-1190 cm^{-1} in metal β-diketonate and appearance of $C\equiv N$ stretching band in the region 2165-2155 cm^{-1}, except for $Cr(CNS\text{–}DBM)_3$ at 2085 cm^{-1} which is interpreted as being due to possible isomerization to isothiocyanate, at the same time provides strong evidence for the thiocyanato group entering at the central carbon atom of each chelate ring. That the electrophilic substitution in the phenyl rings will not be favoured is to be expected from resonance interaction of the phenyl rings with the chelate rings and consequent deactivation of the former. The effect of replacing methyl groups of thiocyanated acetylacetonates by phenyl groups on $C=O$ and $C=C$ absorption bands and perhaps on other bands also is almost the same as in the case of replacements in acetylacetonates. The C–S stretching frequency in the region 725-710 cm^{-1} could not be identified due to serious overlap of other bands in this region. Assignments for some other bands are given on the same basis as for nitro chelates[4] and unsubstituted chelates. Distinct absorption bands in the regions 1345-1330 cm^{-1} and 1075-1050 cm^{-1} observed in all the thiocyanated chelates are not present in the spectra of original chelates. In a few regions assignments of frequencies has not been possible because of the absorption by the phenyl rings in the same region.

The electronic spectral data on metal β-diketonates and their thiocyanated derivatives are recorded in Table III. No bathochromic shift is observed in the electronic spectra of thiocyanated metal chelates. This should be expected, if bulky groups at the ortho positions throw the $C\equiv N$ group out of plane of the ring, preventing resonance interaction of the $C\equiv N$ group with the chelate ring.

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