

The Syntheses of Bisdithiobenzoylacetonates and Its Halogeno Derivatives from Dithiolium Salt*¹

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The dithio-derivatives of β -diketonates have very interesting properties and have previously been reported,¹⁻⁵ but all of them were then synthesized from metal β -diketonate. As the dithio- β -diketonates are so easily dimerized that their monomers have not yet been isolated, these complexes are synthesized by trapping the newly-forming dithio- β -diketone by metal ions before the dimerization occurs.

The present authors previously obtained the dithiolium salts by the method of Schmidt and Schulz from β -diketonates,⁶ and using the 3-methyl-5-phenyl-1,2-dithiolium perchlorate, the syntheses of some dithio- β -diketonates and halogeno-dithio- β -diketonates have been successful. The bis(dithiobenzoylacetonato)cobalt(II) was synthesized from a mixture of anhydrous cobalt(II) chloride and dithiolium salt by a reduction reaction using sodium borohydride under ice cooling; the product was extracted with chloroform. The nickel(II) complex was obtained by a similar method. The trichloro-dithiobenzoylacetonatozinc(II) was synthesized by the reaction of anhydrous zinc(II) chloride and the dithiolium salt in a concentrated hydrochloric acid medium under ice cooling. Other chloro- or bromo-derivatives of the ML_2X_4 and MLX_3 types were obtained by almost the same method. The chemical formulas of the products and their magnetic moments, measured by the Gouy balance method at room temperature, are shown in Table 1. The infrared spectroscopic results of typical compounds are shown in Table 2.

NiL_2 (where HL =dithiobenzoylacetonate) obtained by this method was the same as that reported in a previous paper⁴) and was isostructural to CoL_2 . The CoL_2Cl_4 thus obtained was identical with that reported previously,⁴) while the other three ML_2X_4 -

TABLE 1. CHEMICAL FORMULAE OF COMPLEXES CALCULATED FROM THE ANALYSIS AND THE MAGNETIC MOMENTS

(Figures are given in B.M. per 1 mol of metal.)

NiL_2	dia	CoL_2Cl_4	4.63
CoL_2	not measured	CoL_2Br_4	4.64
$MnLCl_3$	6.01	CuL_2Br_4	1.34
$CuLCl_3$	2.09	CdL_2Cl_4	dia
$ZnLCl_3$	dia		

dia=diamagnetic

HL=dithiobenzoylacetonate ($C_{10}H_{10}S_2$)

TABLE 2. FREQUENCIES FOUND ABOUT THE COMPLEXES IN INFRARED REGION (Figures are given in cm^{-1} .)

CoL_2	CdL_2Cl_4	$MnLCl_3$
	1590 w	1600 m
1470 s	1493 w	1495 w
1462 sh	1470 s	1478 s
1445 s, sh	1445 sh	1453 w
1360 m	1374 w	1376 w
1344 w	1340 m	1336 m
1293 m	1315 w	1315 w
1270 m	1250 s	1253 s
1220 s	1220 w	1218 w
1210 w		
1180 w		
1157 m	1148 m	1148 m
1108 w	1095 m	1098 m
1075 m	1067 w	1075 w
1025 m	1014 m	1015 m, br
1018 m		
999 m	994 s	995 s
967 w	970 w	973 w
907 w	924 m	928 m
867 w	870 s	870 s
857 m	845 w	840 w
760 s	760 s	767 s
737 s		
693 m	707 w	707 w, sh
	680 s	680 s

type complexes seem to be isostructural. The general properties of the MLX_3 -type complexes resemble ML_2X_4 -type ones.

The further application of this method is now going to be studied in our laboratory; the results will be published elsewhere.

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