Infared Investigation of Aromatic and Aliphatic Dithioacids as Ligands. Part I. Metal Dithiobenzoates

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I.r. spectra are reported for a series of dithiobenzoato-complexes of divalent (Ni^{II}, Pd^{II}, and Pb^{II}) and trivalent (Cr^{III}, Fe^{III}, Rh^{III}, and In^{III}) metals and of some of their deuteriated analogues. The two stretching frequencies of the dithiocarboxylic group have been located in the range 900—1000 cm^{-1}, and the metal–sulphur stretchings between 300 and 400 cm^{-1}. The regular decrease of the highest substituent–sensitive frequency of the phenyl group with the optical electronegativity of the chelated metal ion is discussed.

AMONG dithioacid–metal complexes, xanthates and dithiocarbamates have been extensively investigated by i.r. spectroscopy, but, as pointed out by Coucouvanis in a recent review,[1] few papers have been published on metal complexes of dithioacids of general formula RC(S)SH, where R = alkyl or aryl.

This paper deals with the dithiobenzoates of Ni^{II}, Pd^{II}, Pb^{II}, Cr^{III}, Fe^{III}, Rh^{III}, and In^{III} ($PhCSS^-$, dtb) and with some pentadeuteriodithiobenzoic acid derivatives ($C_6D_5CSS^-$, dtb-d), namely $Ni(dtb\text{-}d)_2$ and $Pd(dtb\text{-}d)_2$, because the spectral comparison between the corresponding light and heavy benzene derivatives gives substantial support to the proposed assignments.

I.r. spectra of dithiobenzoates have been investigated by Uhlig and Uebel,[2] who proposed an assignment for Pb^{II}, Cd^{II}, and Tl^{I} complexes, and by Fackler and co-workers [3] who presented the spectrum of $Ni(dtb)_2$ in the region 300—900 cm^{-1}. Recent works by Lindner and co-workers [4] on some dithiobenzoato-complexes of Re^{I} and Mn^{I} give a vibrational assignment (supported by Raman data) which does not agree with that proposed by Uhlig and Uebel.[2]

EXPERIMENTAL

All the non-deuteriated complexes have been supplied by Furlani and co-workers. $Ni(dtb\text{-}d)_2$ and $Pd(dtb\text{-}d)_2$ were prepared as described elsewhere,[5] from C_6D_6 (isotopic purity 99%).

I.r. measurements were made on mulls with a Beckmann IR9 (400—1600 cm^{-1}) and with a Perkin-Elmer 521 (200—450 cm^{-1}). Mulling agents were Nujol (200—1350 cm^{-1}) and Fluorolube (1300—1600 cm^{-1}).

Liquid-nitrogen temperature spectra were taken on KBr pellets, in a conventional low-temperature cell, in the range 400—1600 cm^{-1}.

DISCUSSION

Vibrational Analysis.—By analogy with the structures of $Ni(dtb)_2$,[6] $Pd(dtb)_2$,[7] and $Cr(dtb)_3$,[8] the 1 : 2 complexes should be planar (symmetry D_{2h}), while the 1 : 3 complexes should have D_3 symmetry.

On the basis of the D_{2h} symmetry, the 81 normal modes of $M^{II}(dtb)_2$ can be distributed among the symmetry classes of this group, and among the phenyl groups and the MS_4C_2 moiety as indicated in Table 1. Only the B_{1u}, B_{2u}, and B_{3u} vibrations are i.r.-active. Furthermore, since ω_1, ω_2, ω_3, ω_{15}, and ω_{16} [9] consist of vibrations involving stretchings of the phenyl C–H bonds, which have not been taken into account in the present work, we can expect 32 bands arising from the 11 B_{1u} + 9 B_{2u} + 12 B_{3u} i.r.-active normal modes.

TABLE 1

Distribution of vibrational modes for $M^{II}(dtb)_2$ (D_{2h}) vib-$[M^{II}(dtb)_2] = 14A_g + 4B_{1g} + 13B_{2g} + 8B_{3g} + 5A_u + 14B_{1u} + 9B_{2u} + 14B_{3u}$

Mode [a]	Representation
ω_1—ω_{30}	$11A_g + 11B_{1u} + 3B_{1g} + 3A_u + 10B_{2g} + 10B_{3u} + 6B_{3g} + 6B_{2u}$
ν(C–S)	$A_g + B_{2g} + B_{1u} + B_{3u}$
δ(CSS)	$A_g + B_{1u}$
ν(M–S)	$A_g + B_{2g} + B_{1u} + B_{3u}$
tw(CSS)	$B_{1g} + A_u$
$\rho_{i.p.}$(CSS)	$B_{2g} + B_{3u}$
$\rho_{o.p.}$(CSS)	$B_{3g} + B_{2u}$
$\rho_{o.p.}$(MSS)	$B_{3g} + B_{2u}$
$def._{i.p.}$	B_{3u}
$def._{o.p.}$	A_u
$def._{o.p.}$	B_{2u}

[a] Normal vibrations ' localized ' in the phenyl groups numbered according to Schmid *et al.* (ref. 9); for the description of modes see also J. R. Scherer, *Spectrochim. Acta*, 1963, **19**, 601 and 1965, **21**, 321. Symbols have the following meaning: ν = stretching; δ = deformation; tw = twisting; ρ = rocking; i.p. = in the plane of $C_6H_5CSS^-$; o.p. = out of the plane of $C_6H_5CSS^-$; def. = deformation of the whole molecule, not ' localized ' in a particular group.

The distribution of the 123 normal modes of the $M^{III}(dtb)_3$ molecule among the symmetry classes of the D_3 group, and among the different atomic groupings in the molecule, is indicated in Table 2. Since only vibrations of A_2 and E species are i.r.-active and the C–H stretchings of the phenyl group give rise to $5E + 3A_1 + 2A_2$ vibrations, we can expect only 56 fundamental absorptions ($36E + 20A_2$).

Since the number of bands observed in the range investigated in the present work, both for 1 : 2 and 1 : 3

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[1] D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **10**, 233.

[2] E. Uhlig and E. Uebel, *Z. anorg. Chem.*, 1965, **337**, 98.

[3] J. P. Fackler, jun., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1968, **90**, 2784.

[4] (*a*) E. Lindner, R. Grimmer, and H. Weber, *J. Organometallic Chem.*, 1970, **23**, 209; (*b*) E. Lindner and R. Grimmer, *ibid.*, 1970, **25**, 493.

[5] (*a*) C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586; (*b*) A. Flamini, C. Furlani, O. Piovesana, and A. Sgamellotti, unpublished data; (*c*) O. Piovesana and C. Furlani, *Chem. Comm.*, 1971, 256; (*d*) O. Piovesana and C. Cappuccilli, *Inorg. Chem.*, in the press.

[6] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 324.

[7] M. Bonamico and G. Dessy, *Chem. Comm.*, 1968, 483.

[8] (*a*) M. Bonamico and G. Dessy, *Ricerca sci.*, 1968, 1106; (*b*) E. B. Wilson, J. C. Decius, and P. C. Cross, ' Molecular Vibrations,' McGraw-Hill, New York, 1955, p. 333.

[9] E. W. Schmid, J. Brandmüller, and G. Nonnenmacher, *Z. Electrochem.*, 1960, **64**, 726.

complexes, is higher than that indicated by molecular vibrational analysis, it has been considered important to carry out a crystal vibrational analysis on Pd(dtb)$_2$ and Ni(dtb)$_2$, in order to recognize the number of bands arising from crystalline effects and collect them in groups, each group being referred to a particular molecular mode. The aim was to collect enough information to extend the interpretation to all the other compounds.

TABLE 2

Distribution of vibrational modes for M^{III}(dtb)$_3$ (D_3)

vib[M^{III}(dtb)$_3$] = $19A_1 + 22A_2 + 41E$

Mode [a]	Representation
ω_1—ω_{30}	$30E + 14A_1 + 16A_2$
ν(C–S)	$2E + A_1 + A_2$
δ(CSS)	$E + A_1$
ν(M–S)	$2E + A_1 + A_2$
tw(CSS)	$E + A_1$
$\rho_{i.p.}$(CSS)	$E + A_2$
$\rho_{o.p.}$(CSS)	$E + A_2$
$\rho_{o.p.}$(MSS)	$E + A_2$
def.	$E + A_1$
def.	$E + A_2$

[a] Symbols have the same meaning as in Table 1.

Pd(dtb)$_2$ and Ni(dtb)$_2$ are both monoclinic, space groups $P2_1/c$ [7] and $P2_1/n$,[6] respectively, with 6 molecules per unit cell, 2 on equivalent sites C_i and 4 on equivalent sites C_1. As indicated by the correlation charts,[8b] the molecules with C_i symmetry give rise to five more i.r.-active modes than 'free' molecules, because the A_u modes of D_{2h} become active under C_i. Molecules with C_1 symmetry give rise to 81 absorptions since even g-type molecular vibrations become active under C_1. Thus, most of the molecular modes (except the three last deformations in Table 1) should appear as a triplet of bands, one being due to molecules with C_i symmetry, the other two to molecules with C_1 symmetry.

Furthermore, each of these bands should split in a doublet under factor group field. However, this effect is, in general, less important. In fact, for each molecular normal mode, we observed only three absorptions, even at low temperature and under high resolution.

Spectra and Assignments.—The room-temperature spectra of Ni(dtb)$_2$ *vs.* Ni(dtb-d)$_2$, in the region 400—1600 cm^{-1}, are shown as an example in Figure 1. In

TABLE 3

Infrared frequencies [a] (cm^{-1}) and assignments [b] of Ni(dtb)$_2$, Pd(dtb)$_2$, and their deuteriated analogues (liquid-nitrogen temperature data only in the range 400—1600 cm^{-1})

Assignments	Ni(dtb)$_2$		Ni(dtb-d)$_2$		Pd(dtb-d)$_2$	Pd(dtb)$_2$
ω_{18}	(1591) 1589m		1556m (1553)		1556m (1553)	1590m
ω_4	1586w		1551w (1545)		1550w (1545)	1587m (1579)
ω_5	1484w		1375m 1373m		1374m 1371m	1486w
ω_{19}	1450s 1446s		1331s 1329s		1331mw 1330m	(1449) 1446s
ω_{20}	1337w 1329w		1054vs 1051s 1049m		1053s 1050m	1335w
ω_{17}	(1317) 1315m (1312)		1251vw		1250vw	1318w 1314m (1310)
n.a.	(1300)		1300vvw		1300vvw	(1300)
ω_6	(1270) 1262vs (1259)		(1220) 1217vs		1222s 1221s 1216vs 1212s	1273s 1266vs (1259)
n.a.	(1248)		1242vvw		1241vvw	(1240)
n.a.	(1226)					(1218)
n.a.			(1200)		1202vvw	1202vvw
ω_7	1183m		865w		866w (863) 858vw	1183m (1173)
ω_{21}	1157w		843mw 840m		844vw 841w 839w	1158w
ω_{22}	1099vw 1074vvw	ϕ	824m (821)	ϕ	827vw 823w (821)	1095vw 1074vvw
ω_8	1048vvw 1029vw 1027vvw		(817) 815m		817w (816)	1046vvw 1038vvw 1032vvw
ω_9	(1001) 1000m (998)		959mw 954mw		958vw 955w	1002m (1000)
ω_{12}	995vvw					995vvw
ν_a(CSS)	990m 983vs 975vs		973vs 972vs 967s		(972) 971s (965) 961s	(983) 980vs 973s
ω_{25}	(963)	ϕ	824m (821)	ϕ	827vw 823w (821)	964m
ν_s(CSS)	949m (947) 941m		937m 930w		(938) 937m 927w	947m 944mw
ω_{26}	925w 920m (913)	ϕ	(774) 773m (772)	ϕ	777w 773w 770w	929vw 922w (919)
ω_{10}	848w	ϕ	(774) 773m (772)	ϕ	777w 773w 770w	848mw 839w
ω_{13}	801vvw		663vw (661)		659vw 657vw	800w
ω_{27}	771w 763s 757m		651w 649mw		652w 650w	771m 765m 760s
ω_{28}	683mw 679mw 676m	ϕ	515m 510mw 507s (503)	ϕ	519w 517m 511w 507s	683m 677m 672s
δ(CSS)	673m 667m 663mw		641m 638mw		640m 638w	665m
ω_{23}	(624) 611vw (598)		552m 550m 547mw		558mw 553w 550mw	640vw 630vw 615vw
ω_{11}	566w 559w	ϕ	515m 510mw 507s (503)	ϕ	519w 517m 511w 507s	577w 569w
ω_{29}	434m		432m		434m	439m (420)
ω_{14}	399w	ϕ	371m (359)	ϕ	368mw 362mw	399w
ν_a(MSS)	371ms	ϕ	371m (359)	ϕ	368mw 362mw	372w
ν_s(MSS)	346w		342w		334m 324m	336s 326ms
ω_{24}	247					

[a] vs = Very strong; s = strong; ms = medium strong; m = medium; w = weak; vw = very weak; vvw = very very weak; n.a. = band not assigned; values in parentheses are shoulders. [b] The meaning of symbols is the same as in Table 1. ϕ = Frequencies used again.

Figure 2 are given the spectra of these same compounds in the range 200—450 cm^{-1}. The spectral data and assignments for light and heavy Ni and Pd complexes are listed in Table 3, while the most specific frequencies and assignments for all non-deuteriated compounds under examination are listed in Table 4. Discussion and assignments, unless explicitly specified, will be restricted to the absorptions of Ni and Pd dithiobenzoates, along with their deuteriated analogues.

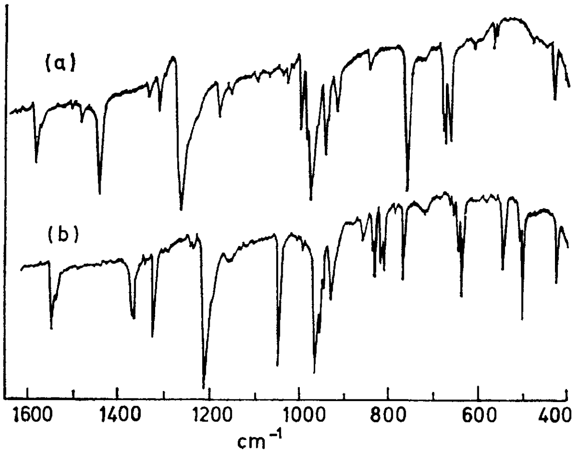

FIGURE 1 Infrared absorption spectra of (a) Ni(dtb)$_2$ and (b) Ni(dtb-d)$_2$) in the range 400—1600 cm^{-1}

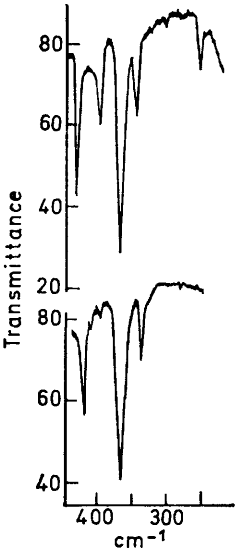

FIGURE 2 Infrared spectra of (a) Ni(dtb)$_2$, (b) Ni(dtb-d)$_2$, in the range 200—450 cm^{-1}

The spectral comparison of all the complexes investigated in this work indicates that, with respect to the behaviour under phenyl-group deuteriation and the change of the co-ordinated metal, the i.r. absorptions can be divided in two classes. In the first class there are bands which are almost unaffected by changing the metal ion, which shift appreciably under phenyl-group deuteriation. In the second class there are bands which are affected in a similar way both by phenyl-group deuteriation and by the change of the co-ordinated metal ion. It is reasonable to expect that the first group of absorptions is formed by most of the phenyl-group vibrations. The remaining bands may arise from chelate ring vibrations, or from some phenyl ring vibration which, owing to its character, is affected both by deuteriation and conjugative effects with the chelate ring.

TABLE 4

Infrared frequencies (cm^{-1}) and assignments[a] of the characteristic absorptions of some metal dithiobenzoates

Assignments	Pb(dtb)$_2$	Cr(dtb)$_3$	Fe(dtb)$_3$	Rh(dtb)$_3$	In(dtb)$_3$
ω_6	1214vs	1246vs	1261vs	1265vs	1225vs 1220vs
ν_a(CSS)	(982) 979vs (974)	988vs 984vs (974)	985m	987ms	992vs 985vs (972)
ν_s(CSS)	913s	934s (927)	946m	947ms	935w 923ms
δ(CSS)	657s	661s	664m	664m	655m
ν_a(MSS)	363w	370m (363)	331w	330w 313w	355w
ν_s(MSS)	311m	354m	320w	302w	324m

The absorptions belonging to the first group will not be discussed in the present work since both their frequencies and intensities, along with those of their deuteriated analogues, agree, in general, with those observed in other light and heavy monosubstituted benzenes.[10] These frequencies are reported in Table 3 with the corresponding assignments (for symbolism, see Table 1). The remaining absorptions, which are more specific of the present compounds, consist of seven medium-to-strong bands at about 1250, 980, 945, 660, 440 cm^{-1} and, the remaining two, in the region 300—370 cm^{-1}.

On the basis of the literature data, the band at 1250 cm^{-1} can be assigned either to the highest substituent-sensitive frequency of the phenyl group,[9] ω_6, or to a vibration which consists mainly of ν_a(CSS). In fact, in monosubstituted benzenes, ω_6 is normally found in the region 1000—1200 cm^{-1}, while, on the other hand, a band at about 1250 cm^{-1}, observed in some dimethyldithiocarbamates[11] and dithiobenzoates,[3,5] has been assigned to ν_a(CSS).

In the present case, however, the experimental evidence indicates that the band *ca.* 1250 cm^{-1} can be correctly assigned to a vibration described chiefly as ω_6. In fact, the shift of *ca.* 40 cm^{-1} undergone by this band under phenyl ring deuteriation would be too relevant for ν_a(CSS), while it is of the same order of magnitude as

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[10] Works chiefly taken into consideration for the present assignments are, as follows: (*a*) R. R. Randle and D. H. Whiffen, Report Conf. Mol. Spectroscopy, 1954, Inst. Petroleum, Paper No. 12; (*b*) D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350; (*c*) R. J. Jakobsen, *Spectrochim. Acta*, 1965, **21**, 127; (*d*) T. R. Nanney, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, 1965, **21**, 1495; (*e*) T. R. Nanney, E. R. Lippincott, and J. C. Hamer, *Spectrochim. Acta*, 1966, **22**, 737; (*f*) T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, 1968, **24**, *A*, 1705; (*g*) W. D. Mross and G. Zundel, *Spectrochim. Acta*, 1970, **26**, *A*, 1109; (*h*) W. D. Mross and G. Zundel, *Spectrochim. Acta*, 1970, **26**, *A*, 1097.

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that observed for ω_6 in many heavy monosubstituted benzenes.[10] Furthermore, dithiobenzoic acid [12] shows a strong absorption at 1250 cm^{-1} which can be correlated only with ω_6. In fact, the alternative assignment, ν(C=S), can be ruled out because, under complex formation, this band should be shifted to lower instead of to higher frequencies, as, in contrast, is observed in Ni(dtb)$_2$ and Pd(dtb)$_2$. Also, this assignment is supported by the presence of an analogous absorption at 1185—1210 cm^{-1} in all thiobenzoate esters, in thiobenzoic acid and in its potassium salt.[13]

As it is known, the two stretching frequencies of the carboxylate ion, normally observed at 1550—1610 and 1400 cm^{-1},[14,15] fall in the range between ν(C=O) (1720 cm^{-1}) and ν(C–O) (which takes part to two absorptions at 1420 and 1200—1300 cm^{-1} [15]). Therefore, it seems reasonable to find the two stretching frequencies of the dithiocarboxylic group in the range 949—1060 cm^{-1}, *e.g.* between ν(C=S) of dithiobenzoic acid [12] and ν(C–S) of thiobenzoic acid.[13] Hence, we are induced to assign the bands at about 980 and 945 cm^{-1} to ν_a(CSS) and ν_s(CSS), respectively.

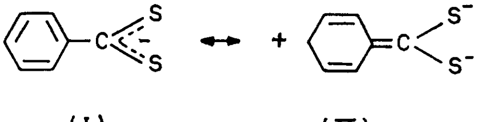
While the assignment of ν_a(CSS) is, in general, in agreement with those previously reported for analogous compounds, some questions arise about the assignment of ν_s(CSS). In fact, most of authors locate the band corresponding to ν_s(CSS) around 600 cm^{-1}.[5,16,17] Indeed, we observed a band of relevant intensity *ca.* 670 cm^{-1} in all the compounds under examination. But, if it would be ν_s(CSS), the band at 945 cm^{-1} should be necessarily assigned to the second substituent-sensitive frequency of the phenyl group, as proposed by Uhlig [3] and Murthy.[18] However, this alternative assignment is in conflict with the small shift exhibited by the band at 945 cm^{-1} under deuteriation ($<$10 cm^{-1}), much smaller than those commonly observed for ω_{10}. In addition, the frequencies reported in the literature for ω_{10} do not exceed the value of 852 cm^{-1} observed by Green in nitrobenzene.[14] On the other hand, the frequency of ν_s(CSS) must be certainly higher than 700 cm^{-1}, where ν(C–S) of sulphides and mercaptans is commonly found. Hence, we are induced to assign the band *ca.* 945 cm^{-1} to a vibration which is mostly described as ν_s(CSS).

The absorption at 670 cm^{-1} is tentatively assigned to δ(CSS). This frequency is surprisingly near to those reported for δ(COO) (673—678 cm^{-1} in alkali-metal benzoates [14]) and δ(CSO) (646—665 cm^{-1} in metal monothiobenzoates [19]).

The assignments of the absorptions found at 850, 570, and 430 cm^{-1} to three of the substituent-sensitive frequencies of the phenyl group, ω_{10}, ω_{11}, and ω_{20} are tentative, but are in agreement (with the exception of ω_{11}) with those proposed by Green for benzoates.[14]

There is little doubt that the two intense absorptions observed between 300 and 370 cm^{-1} in all the compounds under examination arise chiefly from metal–sulphur stretching.[20] In particular, the absorptions observed at 371 and 346 cm^{-1} in Ni(dtb)$_2$, assigned in the present work to the Ni–S stretchings, are remarkably close to those of analogous assignment, found at 383 and 351 in Ni(ethyl xanthate)$_2$,[16] as it is expected from the similarity in bond lengths and geometry of the chelate rings of Ni(dtb)$_2$ [6] and Ni(ethyl xanthate)$_2$.[21] Metal–sulphur stretchings for the other complexes have been assigned by spectral comparison with Ni(dtb)$_2$.

The decrease in frequency of ω_6 along the series Pd $\simeq$ Ni $>$ Pb and Rh $>$ Fe $>$ Cr $>$ In apparently parallels the decrease of the affinity of the metal ion for sulphur [22] and of the optical electronegativity reported by Jørgensen: [23] Pd$^{\mathrm{II}}$ (2·2—2·4) $>$ Ni$^{\mathrm{II}}$ (2·2) and Rh$^{\mathrm{IIII}}$ (2·3) $>$ Fe$^{\mathrm{III}}$ (2·1) $>$ Cr$^{\mathrm{III}}$ (1·8—1·9).* Furthermore, the trend of this frequency is the same as that of the second or third ionization potentials, which decrease as follows (values in parentheses are given in eV): [24] Pd (19·42) $>$ Ni (18·15) $>$ Pb (15·028) and Rh (31·05) $>$ Cr (30·95) $>$ Fe (30·64) $>$ In (28·03). This result can be explained by assuming that resonance structure (II) becomes more important with respect to (I) as the electron withdrawing tendency of the metal ion increases. This latter can be reasonably related to the optical electronegativity or to the second or third ionization potential of the coordinated metal.



(I) (II)

I thank Professor Furlani for providing most of the complexes investigated and for helpful discussions.

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* Values for Ni$^{\mathrm{II}}$ and Fe$^{\mathrm{III}}$ refer to low-spin complexes, as is the case for Ni(dtb)$_2$ and Fe(dtb)$_3$ (see ref. 2).

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