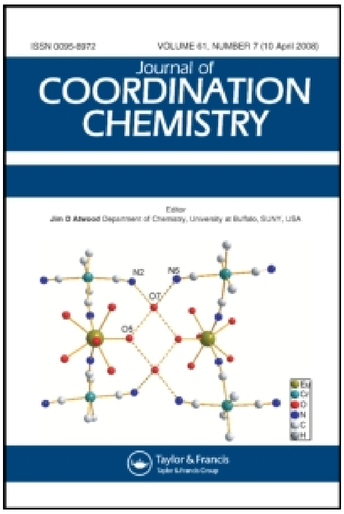

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Peyronel, Giorgio and Fabretti, Antonio C.(1977) 'NICKEL(II) AND COPPER(II) COMPLEXES OF 2,3-DIPHENYL-2,3-DEHYDROTE TRAZOLIUM-5-THIOLATE (DEHYDRODITHIZONE)', Journal of Coordination Chemistry, 7: 2, 119 — 124

To link to this Article: DOI: 10.1080/00958977708073048

URL: http://dx.doi.org/10.1080/00958977708073048

J. Coord. Chem.
1977, Vol. 7, pp. 119–124

NICKEL(II) AND COPPER(II) COMPLEXES OF 2,3-DIPHENYL-2,3-DEHYDROTE TRAZOLIUM-5-THIOLATE (DEHYDRODITHIZONE)

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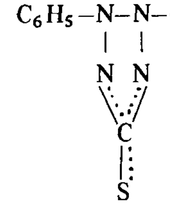
(Received December 21, 1976; in final form March 28, 1977)

The following nickel(II) and copper(II) complexes of 2,3-diphenyl-2,3-dehydrotetrazolium-5-thiolate or dehydro dithizone (L) were prepared: $NiL_2Cl_2 \cdot 2H_2O$, $NiL_7Br_2 \cdot 2EtOH$, $NiL_4I_2 \cdot 2H_2O$, $NiL_2(ClO_4)_2 \cdot 2EtOH$, $CuL_2X_2 \cdot 4H_2O$ (X=Cl,Br) and $CuL_2A_2 \cdot 2H_2O$ ($A=ClO_4$,BF_4). In the nickel complexes the ligand is N-coordinated to the metal. The nickel and copper chloride complexes have a distorted tetrahedral $[ML_2Cl_2]$ coordination with normal magnetic moments. The copper perchlorato and fluoborato complexes have a distorted polimeric six-coordination $[CuL_2A_2]_n$ with bridging S,N-bonded ligand molecules. The other complexes seem to have a tetragonally distorted tetrahedral coordination or two types of chromophores. The subnormal magnetic moments of the copper bromide (1.49 B.M.), perchlorato (0.77 B.M.) and fluoborato (0.83 B.M.) complexes are attributable to metal–metal of superexhange interactions through bridging ligand molecules.

INTRODUCTION

The dithizone derivative $C_{13}H_{10}N_4S$ known as "dehydrodithizone",[1-3]



"anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide,"[4-5] or "2,3-diphenyl-2,3-dehydrotetrazolium-5-thiolate" (DDTT)[6] forms metal complexes in which it normally acts as monodentate S–bonded ligand. Only few complexes of this ligand were known: the solid dimer complexes $[Hg(DDTT)Cl_2]_2$[7] and the complex $Au(DDTT)Cl_3$ identified in solution.[8] In previous works we have investigated the DDTT-complexes of cobalt(II),[9] zinc(II), cadmium(II) and mercury(II),[10] arsenic(III), antimony(III) and bismuth(III);[11] its nickel(II) and copper(II) complexes are studied in this paper.

RESULTS AND DISCUSSION

The nickel(II) and copper(II) complexes of DDTT(L) have the stoichiometries: NiL_2X_2 (X = Cl($2H_2O$)), ClO_4(2EtOH)), $NiL_7Br_2 \cdot 2EtOH$, $NiL_4I_2 \cdot 2H_2O$, $CuL_2X_2 \cdot 4H_2O$ (X = Cl,Br) and $CuL_2A_2 \cdot 2H_2O$ (A = ClO_4,BF_4). In the nickel bromide complex some ligand molecules are not coordinated as in some of the cobalt(II) complexes.[9] In DMF solution the complexes undergo a change of colour. All the i.r. bands of the ligand between 4,000 and 400 cm^{-1} have a composite character.[6] In this spectral region no i.r. band could be attributed to the rocking and wagging modes characteristic for coordinated water molecules.[12-14]

The complex $NiL_2Cl_2 \cdot 2H_2O$ has a magnetic moment (3.24 B.M.) in the range of values given for a distorted tetrahedral coordination.[15] Its electronic spectrum (Table II) agree well with this stereochemistry showing a rather strong unique ν_2 band at 7.41 kK and a ν_3 band split into two rather strong bands at 14.35 and 15.20 kK with two weak bands at 13.33 and 18.18 kK assignable to spin-forbidden transitions.[16] The Dq, B and β values obtained from the ν_2 and averaged $\bar{\nu}_3$ energy values[17] agree well with those of the $NiCl_4^-$ ion (Dq = 409, B = 794, β = 0.76).[16] The far i.r. spectrum shows two very strong ν(NiCl) terminal bands at 293 and 285 cm^{-1} and a rather strong shoulder at 271 cm^{-1} assignable to ν(NiN) mode, in agreement with other ν(NiN) values given by ligands comparable to DDTT: 262–265 cm^{-1} in the pseudo-octahedral $NiIz_4X_2$ and distorted tetra-

TABLE I

Analytical data found % (calcd. %); magnetic moment μ_{eff} (B.M.); molar conductivity $\Lambda_M(\Omega^{-1}\text{mole}^{-1}\text{cm}^2)$ in DMF 10^{-3} solution.

	Colour	C	N	H	μ_{eff}	Λ_M
$NiL_2Cl_2 \cdot 2H_2O$	green	46.51(46.31)	16.71(16.62)	3.36(3.59)	3.24	44
$NiL_7Br_2 \cdot 2C_2H_5OH$	green	54.70(54.57)	18.64(18.76)	4.22(3.95)	2.11	11
$NiL_4I_2 \cdot 2H_2O$	light green	45.53(45.73)	16.56(16.41)	3.27(3.25)	3.22	142
$NiL_2(ClO_4)_2 \cdot 2C_2H_5OH$	brown	42.59(41.98)	13.15(13.05)	3.80(3.76)	2.99	92
$CuL_2Cl_2 \cdot 4H_2O$	yellow	43.50(43.64)	15.78(15.68)	3.83(3.95)	1.98	93
$CuL_2Br_2 \cdot 4H_2O$	brown	38.66(38.82)	13.95(13.94)	3.33(3.51)	1.49	39
$CuL_2(ClO_4)_2 \cdot H_2O$	light brown	39.98(39.55)	14.24(14.21)	2.69(2.81)	0.77	98
$CuL_2(BF_4)_2 \cdot H_2O$	light brown	40.24(40.86)	14.22(14.68)	2.91(2.90)	0.83	103

hedral $NiIz_2I_2$ complexes of imidazole,[18] 270–272 cm^{-1} in the tetrahedral $(MIz)_2NiX_2$ (X = Br,I) of 2-methylimidazole.[19] Of the usual donor atoms only sulphur has not been found in a tetrahedral nickel(II) complex.[20]

The complex *$NiL_4I_2 \cdot 2H_2O$* has a magnetic moment of 3.22 B.M. greater than those reported for distorted tetrahedral structures: 2.86 B.M. for the imidazole complex $NiIz_2I_2$,[18] attributed to a considerable splitting of the $^3T_1(^3F)$ ground state due to the distortion, and 2.84 B.M. for the 2-aminobenzimidazole complex $Ni(abi)_2I_2 \cdot 3H_2O$.[21] The electronic spectrum of the iodide is similar to that of the chloride complex except for the presence of a weak but well shaped band at 8.51 kK and a strong band at 21.70 kK, this last being attributable either to the ligand or to charge transfer transitions due to metal–iodine bonding.[22] A tetrahedral structure (Table II) $[NiL_2I_2]L_2 \cdot 2H_2O$ may agree with the lowering of the ν_2 frequency and Dq value with respect to those of the chloride as a consequence of the spectrochemical order I < Cl. A ν(NiI) terminal i.r. band is observed for the iodide at 185 cm^{-1} and the ratio ν(NiI) : ν(NiCl) = 185 : 293(285) = 0.63(0.65) is in the range accepted for complexes having similar coordinations.[23] The ν(NiN) bands at 269 and 260 cm^{-1} confirm that in this complex too the ligand is N-bonded to the metal.

As the ν_2 band in tetrahedral complexes is not usually split,[16] a second trans-tetragonal chromophore $[NiL_4I_2]$ may be present with its $^3B_{1g} \longrightarrow {^3E_g}$ and $^3B_{1g} \longrightarrow {^3B_{2g}}$ transitions at 8.51 and 10.87 kK respectively. The crystal field parameters $D_t(+270)$, $\overset{E}{Dq}(1087)$ and $\overset{A}{Dq}(614)$ calculated with these band energies[16] well agree with those of other tetragonal nickel(II) complexes with four nitrogen donor atoms in the equatorial plane and two axial halide ligands:[16] e.g. in $Ni(py)_4X_2$ (X = Cl,Br) D_t = +283 and 316, $\overset{E}{Dq}$ = 1173 and 1150, $\overset{A}{Dq}$ = 680 and 600.[24] A tetragonally distorted tetrahedral configuration[25] intermediate between the tetrahedral and the tetragonal symmetry may give rise to two non-equivalent chromophores in the same crystal, favoured by different local steric conditions.

In DMF solution $NiL_4I_2 \cdot 2H_2O$ undergoes solvolysis. Its molar conductivity (Λ_M = 142) is in the range (130–170) characteristic of 1 : 2 electrolytes.[26] The electronic spectrum of an almost saturated solution indicates an octahedral coordination of the type $(NiL_{4-n}(DMF)_{2+n}]^{++}$:

$$\begin{array}{ccccccc} & \nu_1 & & \nu_2 & & \nu_3 & \\ ^3A_{2g} & \longrightarrow & ^3T_{2g} & \longrightarrow & ^3T_{1g} & \longrightarrow & ^3T_{1g}(P) \\ & 8.13\text{w} & & 13.24\text{w} & & (20.84\text{sh}) & \end{array}$$

L or C.T. bands	ν_2/ν_1	Dq cm^{-1}	B cm^{-1}	β
22.75s, 26.45s	1.63	813	739	0.710

The electronic spectrum of the complex *$NiL_7Br_2 \cdot 2EtOH$* in the region 28–14 kK is rather flat but very similar to that of the chloride. The band at 6.90 kK is very weak while the shoulder at 11.76 kK is stronger than those of the other nickel(II) complexes in the same region. The strong far i.r. band at 152 cm^{-1} is typical of bromide-bridged nickel(II) complexes,[21,27,28] while the well shaped but medium–weak band at 200 cm^{-1} may be assigned to a terminal ν(NiBr) mode, the ratio ν(NiBr) : ν(NiCl) = 200 : 293(285) = 0.68(0.70) being in the range accepted for complexes with similar coordination.[23] The magnetic moment of 2.11 B.M. observed for this complex, is still lower than the subnormal magnetic moments of 2.20–2.30 B.M. reported for the complexes of 2-isopropyl-imidazole NiL_4X_2[29] considered as high tetragonally distorted. Two chromophores may cohexist in this complex: one

TABLE II

Electronic spectra (cm^{-1}) of the solid ligand and its nickel(II) and copper(II) complexes. For the nickel complexes a tentative tetrahedral assignment and its crystal field parameters (cm^{-1}) are given; for some of them an alternative tetragonal assignment is discussed in the text.

	$\nu_1{}^a$ $^3T_1 \to {}^3T_2$	ν_2 $^3T_1 \to {}^3A_2$		$^3T_1 \to {}^1E$		ν_3 $^3T_1 \to {}^3T_1(P)$	$^3T_1 \to {}^1T_2$	Ligand or C.T. bands	Dq	B	β^b
DDTT = L								20.000sh, 21.740s 25.000s			
$NiL_2Cl_2 \cdot 2H_2O$	3.660	7.410ms		13.330sh	14.350ms	15.200ms	18.180w	19.600w, 23.500wm, 29.400sh	402	801	0.769
$NiL_7Br_2 \cdot 2EtOH$	3.200	6.900w		11.760sh	14.300ms	15.150ms	18.180w	19.600w, 23.000wm, 28.850s	375	810	0.778
$NiL_4I_2 \cdot 2H_2O$	3.000	5.970ms	8.510mw	10.870sh	14.600ms	15.350s		21.700s, 23.900s, 27.000s	323	851	0.817
$NiL_2(ClO_4)_2 \cdot 2EtOH$	3.990	8.440m		12.900sh	17.250sh	18.500sh		27.000s	457	982	0.943
$CuL_2Cl_2 \cdot 4H_2O$		7.840vsb		14.490w				23.420vs, 27.620vs			
$CuL_2Br_2 \cdot 4H_2O$		8.260msb			16.310m,sh	17.760s,sh	18.940s	23.260sh			
$CuL_2(ClO_4)_2 \cdot H_2O$			12.500sh	14.290sh				23.810sh			
$CuL_2(BF_4)_2 \cdot H_2O$			11.770sh	14.330sh				23.810sh			

[a] Calculated values.

[b] B_0 for nickel(II) ion = 1041 cm^{-1} [16]

diamagnetic and the other with a magnetic moment of 2.98 B.M.

In the complex *NiL₂(ClO₄)₂·2EtOH* the perchlorato anion is coordinated as it is shown by the splitting of the ν_3 and ν_4 bands. A strong broad band at 197 cm^{-1} is assignable to ν(Ni–OClO$_3$) mode. This energy, lower than most of the ν(NiO) frequency values, may be due to a weak Ni–OClO$_3$ bond as in the cases of Cu–ONO$_2$, Cu–OSO$_3$ and Ni–ONO$_2$ bonds for which ν(MO) values of 220,[30] 240[31] and 263 cm^{-1},[32] respectively, are reported. The assignment of the electronic spectrum to a tetrahedral symmetry gives the crystal field parameters reported in Table II. An increase of the Dq, B and β values with respect to those of the halides may be in agreement with the order "oxygen donor ligands" > "halides" in both the spectrochemical and nephlauxetic series.[16] The low magnetic moment (2.99 B.M.) could be due to a high distortion or to the cohexistence of two different chromophores.

The copper(II) complexes *CuL₂X₂·4H₂O (X = Cl,Br)* show strong ν(CuX) bands, their ratio ν(CuBr) : ν(CuCl) = 220 : 265 = 0.83 being in the range given for other copper–halide complexes.[33-35] Their frequencies, even if lower than those of most of the copper(II)–halide complexes, are in agreement with those observed for the pseudo-tetrahedral tetrahalo complexes (267, 248 cm^{-1} for CuCl$_4^-$, 216–174 cm^{-1} for CuBr$_4^-$);[35] the tetragonal 1,2,4-triazole complexes Cu(Tzl)X$_2$ (273 and 206 cm^{-1} for the chloride and bromide, respectively[34] and the tetragonal CuenX$_2$ complexes (267 and 187 cm^{-1}).[36] Also the strong band observed at 113 cm^{-1} for the chloride complex corresponds to the band at 118 cm^{-1} assigned to the Cl–Cu–Cl bending mode in CuCl$_4^-$.[35] The anion mass independent bands observed at 245–250 cm^{-1} for all the complexes may be assigned to ν(CuN) mode in agreement with the values observed in the range of 235–275 cm^{-1} for other copper(II) complexes.[30, 34, 35, 37]

The very strong broad band at 7.84 kK for the chloride and the medium-strong band at 8.26 kK for the bromide complex are attributable to a tetragonally distorted pseudo-tetrahedral structure.[30, 37-40] The bromide complex shows, besides the band at 8.26 kK, three rather strong and well shaped bands at 16.31, 17.62 and 18.94 kK which fall into the region (13–20 kK)[34, 41] in which appear the three bands characteristic for a tetragonal coordination of copper(II) and may therefore indicate the coexistence, also in the copper bromide complex, of two distinct chromophores, one tetrahedral and the other tetragonal.

TABLE III
Far infrared spectra (cm^{-1}) of the solid complexes

	$\nu(MX)_t$	$\nu(NiBr)_b$	$\nu(MS)$	$\nu(MN)$	$\nu(MO)_{ClO_4}$	Other bands
DDTT = L						392m, 360sh, 351ms, 305m, 281w, 220ms, 149w, 138sh, 131sb, 90ms, 66s
$NiL_2Cl_2 \cdot 2H_2O$	293vs 285s, sh			271s,sh		387mw, 354sh, 317sh, 225sh, 148wm, 140sh, 124sh, 106wb
$NiL_2Br_2 \cdot 2EtOH$	200mw	152s		272ms		390s, 348sh, 320w, 305sh, 225wb, 94wb
$NiL_4I_2 \cdot 2H_2O$	185mb			269mb 260mb		348sh, 335msb, 312mw, 305sh, 220vw, 85wb
$NiL_2(ClO_4)_2 \cdot 2EtOH^a$				274mb 252mb	197sb	395ms, 346wb, 309vw, 303sh, 282sh, 225vwb, 90wb
		$\delta(ClCuCl)$				
$CuL_2Cl_2 \cdot 4H_2O$	265vsb	113s		252sh		358w, 327sh, 313sh, 285sh, 223sh, 144sh, 84w
$CuL_2Br_2 \cdot 4H_2O$	220sb		343wb	247sh		357sh, 325vw, 303vw, 278vw, 169w, 148w, 85wm
$CuL_2(ClO_4)_2 \cdot H_2O^b$			345wb	244w	222wmb	356vw, 325vw, 303vw, 279w, 148w, 85w
$CuL_2(BF_4)_2 \cdot H_2O^c$			346mb	246w		353sh, 324sh, 303vvw, 278vw, 220w, 146w, 85vw

[a] ClO_4: ν_3 = 1136s,sh, 1105sh, 1080vvs, 1033sh ν_1 = [920m] ν_4 = 620vs, 630sh ν_2 = [486m]

[b] ClO_4: ν_3 = 1137s,sh, 1100sh, 1083vvs ν_1 = [923m] ν_4 = 621s, 634ms ν_2 = [453w]

[c] BF_4: ν_3 = 1126sh, 1072sh, 1048vvs, 1020sh ν_1 = [761vvs] ν_4 = 517m, 528sh ν_2 = [400mw]

in brackets [ ] the bands which coincide with bands of the ligand or of other complexes.

In the complexes $CuL_2A_2 \cdot 2H_2O$ $(A = ClO_4, BF_4)$ both anions are coordinated to the metal, as it is shown by the splitting of their ν_3 and ν_4 i.r. bands (Table III). A weak-medium i.r. band at 222 cm^{-1} of the perchlorate may be assigned to ν(Cu–OClO$_3$) mode in agreement with the above cited values.[30–32] The electronic spectra of these complexes show only two rather weak shoulders in the region 11.8–14.3 kK indicating a rather deformed six-coordination. For the bromide, perchlorato and fluoborato complexes the i.r. band at about 345 cm^{-1}, not present in the i.r. spectrum of the copper(II) chloride complex, is assignable to a ν(CuS) mode in agreement with other literature values,[42] DDTT acting in these three cases as bidentate S,N-bonded ligand. This conclusion is also in agreement with their subnormal magnetic moments probably due to metal–metal interactions[19] or to super-exchange interactions[43] between two copper(II) ions through the bridging ligand molecules.

EXPERIMENTAL

The ligand DDTT was prepared by oxidation of dithizone with potassium hexacyanoferrate(III)[3] and recrystallized from ethanol. All the reagents were of the best chemical grade. Acid used: HCl 37%, HBr 48%, HI 57%, HClO$_4$ 60%, HBF$_4$ 31%.

The compounds were prepared by adding a solution of the metal salt in the solvent indicated below to an ethanolic solution of the ligand (L), and were washed with ethanol and ethyl ether. $NiL_2Cl_2 \cdot 2H_2O$, $NiL_7Br_2 \cdot 2C_2H_5OH$ and $NiL_4I_2 \cdot 2H_2O$: 0.5 mM of the nickel salt in 1.25 ml EtOH + 0.25 ml of the acid to 1 mM L in 30 ml EtOH; the same products are obtained from solutions with Ni:L ratios of 2:1 and 1:1. $NiL_2(ClO_4)_2 \cdot 2C_2H_5OH$: 0.25 mM of nickel perchlorate in 1 ml EtOH to 1 mM L in 76 ml EtOH; the same product is obtained from a Ni:L ratio of 1:1. $CuL_2Cl_2 \cdot 4H_2O$: 1 mM of copper chloride in 1 ml HCl to 1 mM L in 30 ml EtOH 95%; the same product is obtained from a Cu:L ratio of 2:1; $CuL_2Br_2 \cdot 4H_2O$ and $CuL_2A_2 \cdot H_2O$ $(A = ClO_4, BF_4)$: 0.5 mM of copper carbonate in 0.5–2.5 ml of the acid to 1 mM L in 30 ml EtOH.

The compounds were analysed by standard methods (Table I). Molar conductivities were measured with a WTW conductivity bridge at 25°C. Magnetic moments were determined by the Gouy method and correcting the molar susceptivities with the Pascal constants. Infrared spectra (Table II) were recorded on the solids in KBr disks (4000–250 cm^{-1}) and in nujol mulls on polyethylene (500–250 cm^{-1}) with a Perkin Elmer 521 spectrophotometer and in nujol mulls on polyethylene (400–80 cm^{-1}) with a Hitachi FIS 3 spectrophotometer. The electronic spectra (Table 3) were recorded on the solids in nujol mulls on filter paper with a Shimadzu MPS-50L spectrophotometer and on the solutions with a Beckman DK 1A spectrophotometer.

ACKNOWLEDGEMENTS

This work has been supported by a financial aid of the Consiglio Nazionale delle Ricerche (CNR) of Italy.

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