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Synthesis and Studies on Nickel(III) and Copper(III) Complexes of 3-Methyl-, 4-Methyl- And 2,6-Dimethylpiperidine Carbodithioates

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**SYNTHESIS AND STUDIES ON NICKEL(III) AND COPPER(III)
COMPLEXES OF 3-METHYL-, 4-METHYL- AND
2,6-DIMETHYLPYPERIDINE CARBODITHIOATES**

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ABSTRACT

New complexes of trivalent nickel and copper, viz. Ni(III)(Lcdt)₂X (X = Br, I and Lcdt⁻ = 4-methylpiperidinecarbodithioate anion (4-MePipdcdt) and 2,6-dimethylpiperidinecarbodithioate anion (2,6-Me₂Pipdcdt) and Cu(III)(Lcdt)_nX_m (n = 2, m = 1 when X = I and n = 1, m = 2 when X = Br and Lcdt⁻ = the anions: 3-methylpiperidinecarbodithioate (3-MePipdcdt), 4-MePipdcdt and 2,6-Me₂Pipdcdt) have been prepared by oxidation of M(Lcdt)₂ (M = Ni(II) and Cu(II)) with halogen X₂ in suitable media. The complexes have been characterised by elemental analyses, infrared and electronic spectral and room-temperature magnetic susceptibility studies. For nickel(III) carbodithioates either a square-planar or square-pyramidal structure has been assigned and for the copper(III) carbodithioates, the presence of a mixture of singlet (S = 0) and triplet (S = 1) forms of square-planar species has been proposed.

INTRODUCTION

The higher-valent metal ions play important biological roles¹. In continuation of our earlier studies² on the synthesis and characterisation of higher-valent metal ion carbodithioates, we have synthesised additional new types of nickel(III) and copper(III) carbodithioates. The present investigation involves the preparation and characterisation of nickel(III) and copper(III) complexes with carbodithioate ligands (Fig. 1) derived from saturated heterocyclic secondary amines, viz. 3-methylpiperidine, 4-methylpiperidine and 2,6-dimethylpiperidine.

EXPERIMENTAL

Materials and Methods

3-Methylpiperidine, 4-methylpiperidine and 2,6-dimethylpiperidine (Aldrich Chemicals) were dried by refluxing over sodium hydroxide beads. The colourless liquids obtained after distillation were stored over potassium hydroxide beads. Nickel(II) chloride hexahydrate and copper(II) chloride dihydrate, both from BDH, were used as obtained. Acetone, methanol, carbon tetrachloride and diethyl ether, all from BDH, were purified by the usual methods.

Preparation of NaLcdt

1g of amine (LH), viz. 3-methylpiperidine, 4-methylpiperidine (10.20 mmol) or 2,6-dimethylpiperidine (9.01 mmol) was taken in ethanol (25 mL), cooled to 0°C and to this was added slowly a stoichiometric amount of carbon disulphide (0.77 g, 10.21 mmol and 0.69 g, 9.013 mmol respectively) with constant stirring. A cream coloured solid separated. Then an aqueous solution (5 mL) of the stoichiometric amount of sodium hydroxide (0.40 g, 10.20 mmol and 0.36 g, 9.0 mmol, respectively) was added. The solid immediately dissolved. The

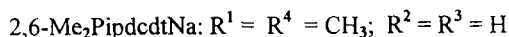
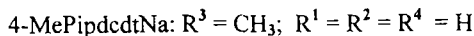
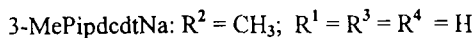
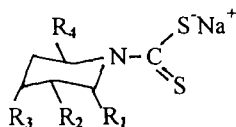


Fig. 1. Sodium Carbodithioates

mixture was then cooled in an ice bath and a precipitate was obtained by addition of excess diethyl ether. The precipitate was filtered and dried in air.

Preparation of Complexes

Ni(Lcdt)₂X [X = Br, I]. An aqueous solution (20 mL) of 0.500 g (2.10 mmol) of nickel(II) chloride hexahydrate was added with stirring to an aqueous solution (30 mL) of a stoichiometric amount of NaLcdt (4.20 mmol). The precipitate of Ni(Lcdt)₂ thus formed was filtered, washed with distilled water and finally with diethyl ether and dried in air. A very dilute solution of bromine or iodine (0.50 mmol) in carbon disulphide (30 mL) was added dropwise to a suspension of Ni(Lcdt)₂ (1.00 mmol) in carbon disulphide (25 mL) with constant stirring till a change in colour of the solution/suspension was noticed. The resulting solution/suspension was stirred at room temperature for 3-4 hours to ensure complete oxidation. The solution of the reaction mixture was concentrated to 1/4th of its volume when the complexes separated out. The complexes were then filtered, washed with carbon tetrachloride followed by ether and finally dried in vacuo.

Cu(Lcdt)_nX_m ($n = 2, m = 1$ when $X = I$ and $n = 1, m = 2$ when $X = Br$). An aqueous solution (20 mL) of 0.500g (2.94 mmol) of cupric chloride dihydrate was added with stirring to an aqueous solution (30 mL) of a stoichiometric amount of NaLcdt (5.88 mmol). A precipitate of Cu(Lcdt)₂ thus formed was filtered, washed with distilled water and finally with diethyl ether and dried in air. A very dilute solution of bromine (1.00 mmol) or iodine (0.50 mmol) in carbon disulphide (30 mL) was added dropwise to the suspension of Cu(Lcdt)₂ (1.00 mmol) in carbon disulphide (25 mL) with constant stirring till a change in colour of the suspension from black to blackish green, was noticed. The resulting suspension was stirred for 3-4 hours to ensure complete oxidation. It was then filtered, washed with carbon tetrachloride followed by ether and finally dried in vacuo.

Note: When a dilute solution of bromine or iodine in carbon disulphide was added dropwise to a suspension of Cu(Lcdt)₂ in carbon disulphide in 1:1 (Cu : X) (X = Br, I) ratio with constant stirring, the product obtained was the same as afforded by the above-given procedure. If a dilute solution of bromine or iodine in carbon disulphide was added dropwise to a suspension of Cu(Lcdt)₂ in carbon disulphide in 1 : 2 (Cu : X) (X = Br, I) ratio a product of undefined composition was obtained.

Elemental Analysis and Physical Measurements

The elemental analyses (Ni/Cu) C, H, N, S and Br/I and the colour of the complexes are given in Table I. Nickel and copper in the complexes were determined volumetrically by EDTA titration using xylenol orange as an indicator. Bromide and iodide were determined volumetrically by Volhard's method and sulphur was determined gravimetrically as BaSO₄. C, H, N determinations, room temperature magnetic susceptibility and IR spectral measurements were made as described earlier³. Electronic absorption spectra

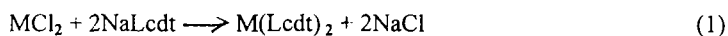
Table 1
Elemental Analyses Data (%) and Colours of the Prepared Sodium Carbothioates and their Complexes

Compound [Formula wt]	M(Ni/Cu)	C	H	N	S	X(Br/I)	Colour	Yield g(%)	Decomposition Temperature(°C)
3-MePipcdtNa (C ₇ H ₁₁ NS ₂ Na) [196]	-	42.41 (42.86)	5.38 (5.61)	7.00 (7.14)	32.15 (32.65)	-	White	1.85 (93)	-
4-MePipcdtNa (C ₇ H ₁₁ NS ₂ Na) [196]	-	42.37 (42.86)	5.32 (5.61)	6.98 (7.14)	32.42 (32.65)	-	White	1.80 (90)	-
2,6-Me ₂ PipcdtNa (C ₈ H ₁₂ NS ₂ Na) [209]	-	45.71 (45.93)	5.62 (5.74)	6.27 (6.69)	30.34 (30.62)	-	White	1.45 (77)	-
Ni(4-MePipcdt) ₂ I (C ₁₄ H ₂₄ N ₂ S ₄ NI) [533]	10.62 (11.03)	31.22 (31.59)	4.04 (4.16)	5.65 (5.26)	24.47 (24.10)	23.77 (23.84)	Brownish green	0.6 (91)	200
Ni(4-MePipcdt) ₂ Br (C ₁₄ H ₂₄ N ₂ S ₄ BrNi) [486]	12.19 (12.10)	34.78 (34.78)	4.67 (4.57)	5.93 (5.77)	25.98 (26.43)	16.78 (16.47)	Brownish green	0.5 (83)	210
Ni(2,6-Me ₂ Pipcdt) ₂ I (C ₁₆ H ₂₈ N ₂ S ₄ NI) [561]	10.06 (10.44)	33.78 (34.18)	4.82 (5.02)	5.28 (4.98)	22.84 (22.81)	23.05 (22.57)	Brownish green	0.55 (85)	210
Ni(2,6-Me ₂ Pipcdt) ₂ Br (C ₁₆ H ₂₈ N ₂ S ₄ BrNi) [514]	11.70 (11.39)	37.34 (37.29)	5.81 (5.47)	5.93 (5.44)	25.17 (24.89)	15.15 (15.50)	Brownish green	0.48 (81)	200
Cu(3-MePipcdt) ₂ I (C ₁₄ H ₂₄ N ₂ S ₄ I) [538.5]	11.29 (11.79)	30.91 (31.17)	3.99 (4.48)	5.59 (5.19)	23.41 (23.79)	23.29 (23.54)	Black	0.52 (80)	200
Cu(3-MePipcdt) ₂ Br ₂ (C ₇ H ₁₂ NS ₂ Br ₂ Cu) [397.5]	16.37 (16.47)	-	-	4.10 (3.60)	15.87 (16.18)	39.92 (40.19)	Purple	0.38 (79)	200
Cu(4-MePipcdt) ₂ I (C ₁₄ H ₂₄ N ₂ S ₄ I) [538.5]	12.19 (11.79)	37.43 (37.17)	3.98 (4.48)	4.88 (5.19)	23.37 (23.79)	23.79 (23.54)	Blackish green	0.55 (85)	210
Cu(4-MePipcdt) ₂ Br ₂ (C ₇ H ₁₂ NS ₂ Br ₂ Cu) [397.5]	15.61 (15.98)	21.58 (21.12)	3.52 (3.04)	3.97 (3.52)	15.99 (16.12)	40.58 (40.19)	Blackish green	0.4 (83)	205
Cu(2,6-Me ₂ Pipcdt) ₂ I (C ₁₆ H ₂₈ N ₂ S ₄ I) [566.5]	11.29 (11.20)	33.75 (33.86)	4.72 (4.98)	5.02 (4.94)	22.91 (22.62)	22.46 (22.39)	Brown	0.55 (86)	200
Cu(2,6-Me ₂ Pipcdt) ₂ Br ₂ (C ₈ H ₁₄ N ₂ Br ₂ Cu) [411.5]	15.06 (15.43)	23.82 (23.32)	3.01 (3.40)	3.36 (3.40)	15.09 (15.57)	38.71 (38.82)	Blackish green	0.35 (75)	200

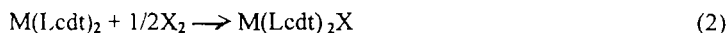
of the complexes as dichloromethane solutions were recorded on a Unicam SP-700 UV-Visible Spectrophotometer in the 1000-2000 nm region. Though the complexes are soluble in some organic solvents, their solutions decomposed within 5 to 10 minutes so that their conductivity measurements and molecular weight determinations were not possible.

RESULTS AND DISCUSSION

The higher-valent nickel(III) and copper(III) carbodithioates (Fig. 2) of the types Ni(III)(Lcdt)₂X (X = Br, I and Lcdt⁻ = 4-MePipdcdt and 2,6-Me₂Pipdcdt) and Cu(III)(Lcdt)_nX_m (n = 2, m = 1 when X = I and n = 1, m = 2 when X = Br and Lcdt⁻ = 3-MePipdcdt, 4-MePipdcdt and 2,6-Me₂Pipdcdt) have been obtained by oxidation of metal(II) carbodithioates, M(Lcdt)₂, with halogen, X₂ [(eq. (2)]. The metal(II) carbodithioates were synthesized by the reaction of metal(II) salt (MCl₂) with an aqueous solution of a stoichiometric amount of sodium carbodithioate [(eq.(1))].

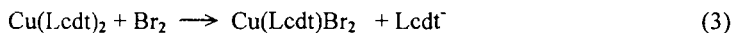


M = Ni(II) and Cu(II)

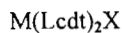


M = Ni(III), X = Br and I and Lcdt⁻ = 4-MePipdcdt and 2,6-Me₂Pipdcdt

M = Cu(III), X = I and Lcdt⁻ = 3-MePipdcdt, 4-MePipdcdt and 2,6-Me₂Pipdcdt

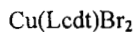
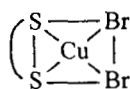


Lcdt⁻ = 3-MePipdcdt, 4-MePipdcdt and 2,6-Me₂Pipdcdt



M = Ni(III); X = Br and I ;

M = Cu(III); X = I



Lcdt⁻: 3-MePipdcdtNa: R² = CH₃; R¹ = R³ = R⁴ = H

4-MePipdcdtNa: R³ = CH₃; R¹ = R² = R⁴ = H

2,6-Me₂PipdcdtNa: R¹ = R⁴ = CH₃; R² = R³ = H

Fig. 2. Proposed Structures of the Complexes

Infrared Spectra

In the IR spectra, the positions of the $\nu_a(SCS)$ and $\nu_s(SCS)$ stretching modes of vibrations of the $>NCS_2$ group of the carbodithioate ligands (at 965-1012 and 885-914 cm^{-1} , respectively) suggest a chelating bidentate mode of coordination to the metal ions⁴. The bidentate mode of the ligand is also supported by C=N stretching frequency. A blue shift in the C=N stretching frequencies for all the carbodithioate ligands of the saturated heterocyclic

amines upon coordination has been observed, thus indicating that these carbodithioate ligands have typical bidentate character^{5,6}. The $\nu(\text{C}=\text{N})$ stretching frequency (Table II) shows an increase of $\sim 60\text{--}85\text{ cm}^{-1}$ compared to the free sodium carbodithioate ligands ($1405\text{--}1438\text{ cm}^{-1}$) with respect to their $\text{M}(\text{Lcdt})_2\text{X}$ and $\text{Cu}(\text{Lcdt})\text{Br}_2$ complexes. The literature² reveals that the $\nu(\text{C}=\text{N})$ stretching frequency shows an increase of about 30 cm^{-1} in going from free sodium dithiocarbamate (1455 cm^{-1}) ligand to the $\text{M}(\text{dtc})_2$ complex (1485 cm^{-1}) and a further increase of $\sim 25\text{--}80\text{ cm}^{-1}$ from $\text{M}(\text{dtc})_2$ to $[\text{M}(\text{dtc})_2]\text{X}$ complex ($\sim 1560\text{ cm}^{-1}$). A significant increase in the $\nu(\text{C}=\text{N})$ value at the second stage indicates the presence of the ligand as dithiocarbamate and not as thiuram disulfide (tds) showing that dithiocarbamate does not undergo oxidation during the synthesis of the higher oxidation state metal complexes. For the present complexes (where the dithiocarbamate ligand has been derived from similar type of heterocyclic bases as those of the reference (2)) the normal metal(II) dithiocarbamates $[\text{M}(\text{dtc})_2]$ have not been obtained and consequently their $\nu(\text{C}=\text{N})$ values not recorded. But the extent of increase in $\nu(\text{C}=\text{N})$ values observed for $\text{M}(\text{dtc})_2\text{X}$ or $\text{M}(\text{dtc})\text{X}_2$ complexes is equivalent to the increase reported in literature for the two stages put together and indicates the presence of the ligand as piperidinecarbodithioates and not as their thiuram disulphide derivatives (tds). The expected $\nu(\text{C}=\text{N})$ values for thiuram disulphides of sodium 3-MePipdcdt, sodium 4-MePipdcdt and sodium 2,6-Me₂Pipdcdt ligands are 1435 , 1465 and 1430 cm^{-1} respectively. These values are much lower than the $\nu(\text{C}=\text{N})$ values for $\text{M}(\text{Lcdt})_{1\text{or}2}\text{X}_{2\text{or}1}$ complexes (Table II), but are higher than those of free sodium carbodithioates, thus showing that the piperidinecarbodithioate ligands do not undergo oxidation during the synthesis of their complexes⁷. This inference is based on the fact that the general trend of rise in the $\text{C}=\text{N}$ stretching frequency follows the order⁸⁻¹²:

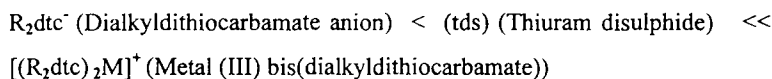


Table II

Room-Temperature $\nu(\text{C}=\text{N})$ Values, Magnetic Moment Values, and Electronic Absorption Spectral Values of Nickel(III) and Copper(III) Carbodithioates

Compound	$\nu(\text{C}=\text{N})$	μ_{eff} (B.M.)	Electronic Absorption Values (nm)
3-MePipdcdtNa	1410	-	-
4-MePipdcdtNa	1438	-	-
2,6-Me ₂ PipdcdtNa	1405	-	-
Ni(4-MePipdcdt) ₂ I	1499	1.93	380, 665, 870
Ni(4-MePipdcdt) ₂ Br	1497	1.96	385, 660, 865
Ni(2,6-Me ₂ Pipdcdt) ₂ I	1470	2.07	380, 660, 860
Ni(2,6-Me ₂ Pipdcdt) ₂ Br	1465	2.54	380, 655, 860
Cu(3-MePipdcdt) ₂ I	1470	1.34	420, 620
Cu(3-MePipdcdt)Br ₂	1495	0.81	365, 542
Cu(4-MePipdcdt) ₂ I	1495	1.67	420, 620
Cu(4-MePipdcdt)Br ₂	1510	0.57	352, 545
Cu(2,6-Me ₂ Pipdcdt) ₂ I	1465	1.62	425, 620
Cu(2,6-Me ₂ Pipdcdt)Br ₂	1475	1.65	430, 590

The appearance of new vibrational bands in the region 400-410 cm^{-1} as compared to that of the free sodium carbodithioate ligands indicates the formation of the higher valent metal-sulphur bonds.

Magnetic Susceptibilities

Nickel(III) ion (d^7) is isoelectronic with divalent cobalt. For all nickel(III) complexes, the μ_{eff} values lie between 1.93 to 2.54 (Table II). These values are much too low as compared to the values (4.8-4.4 B.M.) for a tetrahedral geometry but are very near to the values for the low-spin nickel(III) in either square-planar^{13,15} or square-pyramidal^{16,17} geometry (2.8-2.1 B.M.) around the Ni^{3+} ion (d^7) containing one unpaired electron with considerable orbital contribution. The copper(III) complexes under study have magnetic moment values lying between 1.34 - 1.67 B.M. (Table II) with the exception of $\text{Cu}(3\text{-MePipdcdt})\text{Br}_2$ and $\text{Cu}(4\text{-MePipdcdt})\text{Br}_2$ which show magnetic moments of 0.81 and 0.57 B.M. Generally, copper(III), a d^8 system prefers a low-spin planar geometry with diamagnetic¹⁸⁻²⁰ behaviour, while for tetrahedral system the theoretical magnetic moment (3.9 B.M.) is much too high to correspond to the present copper(III) complexes. The magnetic moment values show an appreciable paramagnetic nature of these complexes when linked to the planar geometry. The anomalous magnetic behaviour of these square-planar complexes can be attributed to the existence of the mixture of singlet ($S = 0$) and triplet ($S = 1$) states, where the singlet is the ground state and the triplet is low-lying excited state. Such type of anomalous magnetic behaviour has already been observed for the isoelectronic, presumably square-planar nickel(II) complexes^{21,22}. Though d^8 square-planar complexes are expected, in general, to be diamagnetic, an equilibrium between spin-free (triplet state - two unpaired electrons would be present) and spin-paired (singlet state - no unpaired electron) configurations is not forbidden, especially if the $d_{x^2 - y^2}$ orbital is not highly destabilised²³, where

the ground state changes from singlet to triplet. Due to closeness of these two levels, there could be a thermal population in both levels which may result in an intermediate magnetic moment as is observed for the present complexes. Low paramagnetism in four-coordinate copper(III) complexes has been reported earlier but there the compounds have been considered to be a mixture of square-planar and tetrahedral species, mainly on the basis of electronic spectral studies¹³. In the complexes $\text{Cu}(3\text{-MePipdcdt})\text{Br}_2$ and $\text{Cu}(4\text{-MePipdcdt})\text{Br}_2$ the low value (0.81 and 0.57 B.M.) of the magnetic moment shows that there is a greater amount of the singlet state and a lesser amount of the triplet state, these low values of magnetic moment could also be due to temperature-independent paramagnetism in a diamagnetic species.

Electronic Spectra

The observation of electronic absorption spectral bands around 380, 660 and 865 nm in the nickel(III) carbodithioates under study indicates square-planar geometry around nickel(III) ion^{24,25}. The electronic absorption spectral values of all the copper(III) complexes are given in Table II. It is reported that tetrahedral nickel(II) complexes give electronic spectral bands at 600 and 900 nm whereas square-planar complexes absorb in the regions 400 and 600 nm^{19,27,28}. Copper(III) is isoelectronic with nickel(II) having $3d^8$ configuration. In the copper(III) carbodithioates under study, the absorbance bands are found to lie around 400 and 600 nm which show square-planar geometry around copper(III) metal ion. In the absence of the quantitative measurements the molar absorptivities for the complexes under study were not obtained. However, the position of the bands in our complexes are about the same as reported earlier for the complex $[(\text{C}_6\text{H}_{11})\text{NCS}_2]_2\text{Cu}]\text{ClO}_4$ for which the molar absorptivities expressed as $(\log \epsilon)$ have been given as 430 nm (4.37) and 645 nm (2.66)¹⁰. These low values of ϵ for the spectral bands are indicative of the absorptions being the d-d bands.

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