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Transition Metal Complexes of α-Naphthylamine Dithiocarbamate

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α-Naphthylamine dithiocarbamate and its complexes with Co(II), Ni(II), Cu(II), Ru(III), Rh(III), Pd(II), Pt(IV), Zn(II), Cd(II) and Hg(II) have been prepared and characterized by chemical analysis, IR — and reflectance spectral studies and magnetic susceptibility measurements. In all these complexes the dithiocarbamato moiety acts as a chelate. The Ni(II), Cu(II) and Pd(II) complexes have been found to be square planar while those of Ru(III), Rh(III) and Pt(IV) were proposed to be octahedral in nature. The Co(II) ion seems to have a tetrahedral geometry, unlike the other known square planar dithiocarbamato complexes of Co(II). No definite structure, however, could be proposed for Zn(II), Cd(II) and Hg(II) on the basis of limited studies.

During the last two decades interest has been invoked in the study of dithiocarbamate complexes of transition metal ions[1-5] and group IV metal halides[6-8], particularly owing to their dual behaviour of acting both as a unidentate ligand and a chelating agent. In our earlier communications, we have reported on the symmetrical and unsymmetrical nature of dithiocarbamato groups. In this paper we are reporting on the study of transition metals with ~~a~~ hitherto unknown α-naphthylamine dithiocarbamate.

EXPERIMENTAL

α-Naphthylamine (B.D.H.) melting at 50 °C was recrystallised from ethyl alcohol. The solvents were purified by conventional methods. Carbon disulphide and sodium hydroxide used were also B.D.H. reagents. Chloroplatinic acid, palladium(II) chloride, ruthenium(III) chloride (Johnson-Matthey), rhodium(III) chloride (Koch-Light) and other metal chlorides (B.D.H. A.R. grade) were used as such.

The IR spectra (4000—200 cm^{-1}) were run on a Perkin Elmer 651 spectrophotometer. The diffuse reflectance spectra were recorded on a Carl-Zeiss VSU-2P spectrophotometer using MgO as calibrant. The magnetic susceptibility measurements were done by the Faraday's Method. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of the Pascal's constants. Elemental analyses were done by the usual microanalytical techniques.

Synthesis of Sodium α-Naphthylamine Dithiocarbamate [(α-NHdtc)·Na]

α-Naphthylamine, carbon disulphide and sodium hydroxide were taken in 1 : 1 : 1 molar ratios respectively. To an ethanolic solution of α-naphthylamine, carbon disulphide and sodium hydroxide were added with continuous stirring. On completion of this reaction a light violet crystalline solid melting at 290 °C, was obtained (yield = 80%). It was soluble in DMF and DMSO.

Preparation of Complexes with Transition Metal Chlorides

The metal dithiocarbamate may be synthesized by one of the following methods. (i) By direct insertion of a $—CS_2$ group in the presence of an amine and the metal chloride (MCl_2 or MCl_3)

$$2\,RHNH + 2\,CS_2 + MCl_2 \longrightarrow (RHNCS_2)_2\,M + 2\,HCl$$

(ii) By a replacement reaction using the sodium salt of the dithiocarbamate

$$2\,(RHNCS_2)\,Na + MCl_2 \longrightarrow (RHNCS_2)_2\,M + 2\,NaCl$$

In the present case the complexes of α-naphthylamine dithiocarbamate were synthesized by the first method. To a mixture of metal chloride in alcohol and carbon disulphide, a solution of α-naphthylamine in the same solvent (in 1 : 2 : 2 or 1 : 3 : 3 molar ratio) was added dropwise. The reaction mixture was stirred for one hour, heated on a water bath for fifteen minutes and then kept overnight. The solid thus obtained was filtered, washed with excess of hot alcohol and dried in vacuum.

RESULTS AND DISCUSSION

The analytical results of the complexes, their colour and melting points are given in Table I. Complexes of the type $M(\alpha\text{-NHdtc})_2Cl_{0-2}$ have been isolated where, M = Co(II), Ni(II), Cu(II), Rh(III), Pd(II), Pt(IV), Zn(II), Cd(II) and Hg(II).

According to Chatt and coworkers[9] the IR spectra of alkyl dithiocarbamates should exhibit a strong band between 1480 to 1550 cm^{-1} assigned to polar $S_2C\div\!\div N$ stretching frequency. This frequency lies intermediate to those associated with the C—N single bond (1250—1350 cm^{-1}) and C=N double bond (1640—1690 cm^{-1}). The $S_2C\div\!\div N$ stretching frequency in aryl dithiocarbamates have been found to lie below the range quoted by Chatt et al.[9], which may be due to the electron withdrawing nature of the aryl group[3]. In the present work the absorption bands observed between the 1370—1380 cm^{-1} region (Table II) have been assigned to $\nu\,C\div\!\div N$ which are consistent with that reported by Coucouvanis and his coworkers[10].

The bands between 1010 cm^{-1} and 1020 cm^{-1} (Table II) have been assigned to the $(C\div\!\div S)$ stretching modes[3]. This $\nu\,(C\div\!\div S)$ band also seems to have partial double bond character as it falls between a C—S single bond (600—800 cm^{-1}), and a C = S double bond (1050—1200 cm^{-1}).

A comparison of the far IR spectra of α-naphthylamine dithiocarbamate and its complexes showed some additional bands besides the usual group frequencies which are essentially due to metal-sulphur and metal-halogen bonds (Table II).

Most dithiocarbamato Co(II) complexes are square planar with the magnetic moment value ranging from 1.60 to 2.5 μ_B[3-4]. The magnetic moment value of ~ 4.79 μ_B dark green colour and the electronic spectral band are the characteristics of a tetrahedral Co(II) complex with sulphur donors[11]. In our green $Co(\alpha\text{-NHdtc})_2$ complex ($\mu_{eff} = 4.69\ \mu_B$) only one absorption band is also indicative of a tetrahedral cobalt (II) ion.

For a tetrahedral Co(II) complex with sulphur donors the $\nu\,(Co — S)$ falls in the 388—390 cm^{-1} region[12] while for a square planar cobalt(II) dithiocarbamate complex[4], it has been noted at 360 cm^{-1}. The $\nu\,(Co — S)$

TABLE I

Analytical Data and Other Physical Properties of α-Naphthylamine Dithiocarbamate Complexes

Complexes	Colour	M. P. °C	Calcd. %C (Obs)	Calcd. %H (Obs)	Calcd. %N (Obs)	Calcd. %S (Obs)	Calcd. %Cl (Obs)	Calcd. %M (Obs)
α-NHdtc · Na	Light violet	290	54.77 (54.91)	3.31 (3.29)	5.80 (5.78)	26.55 (26.70)	— —	— —
Co(α-NHdtc)$_2$	Black	280^d	53.12 (53.19)	3.62 (3.69)	5.63 (5.68)	25.75 (25.82)	— —	11.85 (11.91)
Ni(α-NHdtc)$_2$	Dark green	220	53.14 (53.31)	3.62 (3.64)	5.64 (5.71)	25.76 (25.07)	— —	11.81 (11.61)
Cu(α-NHdtc)$_2$	Black	250	52.63 (52.72)	3.58 (3.64)	5.58 (5.69)	25.54 (25.69)	— —	12.52 (12.69)
Ru(α-NHdtc)$_2$Cl	Black	250	45.94 (46.21)	3.13 (3.14)	4.87 (4.89)	22.27 (22.35)	6.17 (6.05)	— —
Rh(α-NHdtc)$_3$	Dark brown	250	52.11 (51.34)	3.55 (3.56)	5.52 (5.55)	25.26 (25.51)	— —	— —
Pd(α-NHdtc)$_2$	Yellow	245	48.49 (48.64)	3.30 (3.32)	5.14 (5.18)	23.51 (23.59)	— —	— —
Pt(α-NHdtc)$_2$Cl$_2$	Black	250	37.49 (37.77)	2.55 (2.57)	3.97 (3.91)	18.17 (18.29)	10.08 (10.21)	— —
Zn(α-NHdtc)$_2$	Grey	210	52.44 (53.55)	1.57 (1.58)	5.56 (5.68)	25.42 (25.91)	— —	— —
Cd(α-NHdtc)$_2$	Pale yellow	220^d	47.96 (48.86)	3.27 (3.29)	5.08 (5.17)	23.25 (23.38)	— —	— —
Hg(α-NHdtc)$_2$	Grey	280	41.34 (40.31)	2.81 (2.78)	4.38 (4.42)	20.04 (19.18)	— —	— —

^{d} decomposition temperature

TABLE II

IR Spectra (4000—200 cm^{-1}) of α-Naphthylamine Dithiocarbamato Complexes and Their Assignments

Complexes	ν (C$\cdots$N) cm^{-1}	ν (C$\cdots$S) cm^{-1}	ν (M—S) cm^{-1}	ν (M—Cl) cm^{-1}
α-NHdtc · Na	1370vs	1010vs	—	—
Co(α-NHdtc)$_2$	1370s	1010vs	375m	—
Ni(α-NHdtc)$_2$	1375s	1005vs	390m 325w	—
Cu(α-NHdtc)$_2$	1370s	1010s	365s 325m	—
Ru(α-NHdtc)$_2$Cl	1380s	1010vs	340m	325m 315m
Rh(α-NHdtc)$_3$	1370s	1010vs	330s	—
Pd(α-NHdte)$_2$	1370s	1009vs	340s	—
Pt(α-NHdtc)$_2$Cl$_2$	1370s	1009vs	380m	320m
Zn(α-NHdtc)$_2$	1370s	1002s	330m	—
Cd(α-NHdtc)$_2$	1380s	1020m	330m	—
Hg(α-NHdtc)$_2$	1380s	1020m	325s	—

vs = very strong; s = strong; m = medium; w = weak

TABLE III

Magnetic Measurement and Electronic Spectra of α-Naphthylamine Dithiocarbamato Complexes

Complexes	μ_{eff}/μ_B	band position cm^{-1}	Assignment
Co(α-NHdtc)$_2$	4.69	14,705	$^4T_{1g}(P) \longleftarrow {}^4A_{2g}$
Ni(α-NHdtc)$_2$	D	24,390 17,500 15,810	Charge transfer $^1B_{3g} \longleftarrow {}^1A_{1g}$ $^1B_{1g} \longleftarrow {}^1A_{1g}$
Cu(α-NHdtc)$_2$	1.89	25,641 23,000 17,241	Charge transfer $^2A_{1g} \longleftarrow {}^2B_{1g}$ $^2E_g \longleftarrow {}^2B_{1g}$
Pd(α-NHdtc)$_2$	D	27,030 21,000	Charge transfer $^1B_{1g} \longleftarrow {}^1A_{1g}$
Rh(α-NHdtc)$_3$	D	25,641 28,571	$^1T_{1g} \longleftarrow {}^1A_{1g}$ $^1T_{2g} \longleftarrow {}^1A_{1g}$
Pt(α-NHdtc)$_2$Cl$_2$	D	27,777 24,390 16,666	$^1T_{1g} \longleftarrow {}^1A_{1g}$ $^1T_{1g} \longleftarrow {}^1A_{1g}$ $^3T_{2g} \longleftarrow {}^1A_{1g}$

D = diamagnetic

observed at 375 cm^{-1} in this case also supports a tetrahedral geometry for the Co(II) ion.

The complex, [Ni(α-NHdtc)$_2$] and its pyridine adduct were reported by Kaul and Pandeya[13] during the course of this work and it is interesting to note that the results of this work are almost the same as reported by them.

The magnetic moment values and the electronic spectral data (Table III) for Ni(II), Cu(II) and Pd(II) bis (α-naphthylamine dithiocarbamate) are in accordance with other reported square-planar complexes[5].

The diamagnetism of Rh(III) and Pt(IV) is common for octahedral environment[5,14] but the diamagnetic behaviour of Ru(III) is naturally unusual. The spin pairing in this case may be explained by the overlap of suitable metal orbitals yielding in σ or Λ bond formation if the metal ions are very close to each other (as in the case of dimers) or due to the formation of extended molecular orbitals by the extended overlap of the metal and chloride orbitals. It is, of course difficult to choose one of the above two possibilities when deciding on the geometry of the molecule, unless a thorough X-ray structure is determined. However, the diamagnetism can also be explained on the basis of electron interaction through the intervening anions, when there is chlorine bridging, which seems more plausible in the present case. This complex shows only charge transfer bands. This is in accordance with the reported diamagnetic Ru(III) complex[15].

As Zn(II), Cd(II) and Hg(II) have a d^{10} electronic configuration, no d—d transitions are expected in the reflectance spectra of their complexes. On the basis of limited studies no conclusive results pertaining to their geometries could be drawn.

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SAŽETAK

Kompleksi α-naftilamin-ditiokarbamata s prijelaznim metalima

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Pripravljeni su kompleksi α-naftilamin-ditiokarbamata sa Co(II), Ni(II), Cu(II), Ru(III), Rh(III), Pd(II), Pt(IV), Zn(II), Cd(II) i Hg(II) i karakterizirani elementnom analizom, spektrima refleksije i IR-apsorpcije te mjerenjima magnetske susceptibilnosti. U svima ispitanim spojevima ditiokarbamatna skupina djeluje kao kelirajuće mjesto. Koordinacija je u kompleksima Ni(II), Cu(II) i Pd(II) kvadratno-planarna, a u kompleksima Ru(III), Rh(III) i Pt(IV) je oktaedarska; Co(II) pak koordinira se vjerojatno tetraedarski. Nije bilo moguće predložiti tip strukture za komplekse Zn(II), Cd(II) i Hg(II).