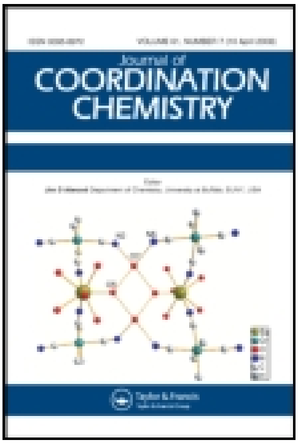
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:32
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Magnetic and spectral studies on nickel(II) and copper(II) dithiocarbazates derived from isoniazid

S.B. Kalia [a], K. Lumba [a] & P. Sankhyan [a]

[a] Department of Chemistry, Himachal Pradesh University, Shimla 171005, India

Published online: 08 Apr 2011.

To cite this article: S.B. Kalia, K. Lumba & P. Sankhyan (2011) Magnetic and spectral studies on nickel(II) and copper(II) dithiocarbazates derived from isoniazid, Journal of Coordination Chemistry, 64:7, 1216-1228

To link to this article: http://dx.doi.org/10.1080/00958972.2011.565414

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry
Vol. 64, No. 7, 10 April 2011, 1216–1228

Magnetic and spectral studies on nickel(II) and copper(II) dithiocarbazates derived from isoniazid

S.B. KALIA*, K. LUMBA and P. SANKHYAN

Department of Chemistry, Himachal Pradesh University, Shimla 171005, India

(*Received 7 August 2010; in final form 24 January 2011*)

Some isonicotinoyldithiocarbazate complexes of nickel(II) and copper(II), of general formulae $M(IN\text{-}Dtcz)_2$, $[M(IN\text{-}DtczH)_2]Cl_2$, and $[M(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$ ($M = Ni(II)$, Cu(II); INDtcz = isonicotinoyldithiocarbazate; IN-DtczH = isonicotinoyldithiocarbazic acid; IN-DtczH-Sal = salicylaldehyde Schiff base of isonicotinoyldithiocarbazic acid), have been synthesized. These complexes have been investigated by elemental analyses, mass, room temperature infrared and electronic spectra, and variable temperature magnetic susceptibility measurements. The three nickel(II) dithiocarbazates and $[Cu(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$ exhibit NS linkage of the ligands, while $Cu(IN\text{-}Dtcz)_2$ and $[Cu(IN\text{-}DtczH)_2]Cl_2$ have ONS binding of the ligands. The nickel(II) dithiocarbazates have $[NiN_2S_2]$ chromophore. Magnetic and solution electronic absorption spectral data reveal square-planar geometry for $Ni(IN\text{-}Dtcz)_2$ and the existence of square-planar–tetrahedral equilibrium for $[Ni(IN\text{-}DtczH)_2]Cl_2$ and $[Ni(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$. Copper(II) dithiocarbazates, namely $Cu(IN\text{-}Dtcz)_2$, $[Cu(IN\text{-}DtczH)_2]Cl_2$, with ONS ligands having dimeric or polymeric octahedral structures, and $[Cu(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$, with NS binding having dimeric square-planar structure, exhibit antiferromagnetism. Superexchange pathway involving the bridging nitrogen and sulfur of the isonicotinoyldithiocarbazate ligands rather than direct metal–metal exchange is suggested for antiferromagnetic interactions. The spin exchange parameter, $-2J = 202.14$ and $29.26\,\mathrm{cm^{-1}}$, has been evaluated for $[Cu(IN\text{-}DtczH)_2]Cl_2$ and $[Cu(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$, respectively, while it could not be evaluated for $Cu(IN\text{-}Dtcz)_2$ because the slope was negative due to the non-variation of its magnetic moment with temperature. The difference in antiferromagnetic behavior and inconsistency of $2J$ for $[Cu(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$ has been attributed to different electronic and steric factors of the three ligands, that is, isonicotinoyldithiocarbazate, its acid, and salicylaldehyde Schiff-base derivative.

Keywords: Isonicotinoyldithiocarbazate; Salicylaldehyde; Nickel(II); Copper(II); Infrared and electronic spectra; Variable temperature magnetic susceptibility

1. Introduction

The chemistry of dithiocarbazates has received considerable attention in view of their unusual physico–chemical properties [1, 2], structural features [3, 4], potentially useful chemotherapeutic properties [5], and relevance to biological systems [6, 7]. Dithiocarbazates of nickel(II) and copper(II) have been widely studied and reported to exhibit antimicrobial [8, 9], antileukemic [10, 11], and anticancer [12–14] properties. The present investigation involves derivatization of heteroaroyl hydrazine, that is,

---

*Corresponding author. Email: shashibalakalia@rediffmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.565414

pyridine-4-carbonylhydrazine, commonly called isoniazid (INH), to obtain the dithiocarbazate ligand. Isoniazid, an antimycobacterial agent, has been used as a front line drug for prophylaxis and chemotherapy of tuberculosis since 1952 [15]. Coordination chemistry of isonicotinoyldithiocarbazate may open up new avenues to improve its chemical, pharmacological, and industrial properties.

2. Experimental

2.1. *Materials and methods*

Isoniazid, metal salts (Merck), and all other chemicals were of analytical grade.

2.2. *Preparation of ligands*

2.2.1. Isonicotinoyldithiocarbazic acid (IN-DtczH). To a continuously stirred methanolic solution (50 mL) of isonicotinic acid hydrazide (1 g, 7.29 mmol) was added dropwise 0.55 g (7.29 mmol) of carbon disulfide giving a light yellow liquid, which was filtered and the filtrate evaporated to dryness on a water bath. This was done to carry out physical measurements of the powder of the acid, that is, IN-DtczH. However, the ligand is obtained *in situ* for the synthesis of metal complexes, because in the solid form the free acid is not stable and decomposes with liberation of carbon disulfide.

2.2.2. Sodium isonicotinoyldithiocarbazate (IN-DtczNa). To a light yellow liquid of isonicotinoyldithiocarbazic acid obtained as above was added a solution of sodium hydroxide (0.29 g, 7.25 mmol) in methanol (50 mL) dropwise with constant stirring. Greenish-yellow solution obtained was filtered and the filtrate was evaporated to dryness on a water bath. This was done to carry out physical measurements of the powder IN-DtczNa. However, the ligand sodium isonicotinoyldithiocarbazate was prepared afresh (*in situ*) for the synthesis of $M(IN\text{-}Dtcz)_2$ ($M = Ni(II), Cu(II)$).

2.2.3. Salicylaldehyde Schiff base of IN-DtczH (IN-DtczH-Sal). To a solution of isonicotinic acid hydrazide (1 g, 7.29 mmol) in methanol (50 mL) carbon disulfide was added with constant stirring (0.55 g, 7.29 mmol), giving a light yellow liquid of isonicotinoyldithiocarbazic acid. To this liquid kept at 40–45°C, a solution of salicylaldehyde (0.89 g, 7.27 mmol) in methanol (20 mL) was added dropwise with constant stirring. The resulting solution was further stirred for 30 min when a creamish-white solid separated. It was filtered, washed with methanol, and dried in air. Final drying was done by keeping the solid overnight in a $CaCl_2$ desiccator.

2.3. *Preparation of complexes*

2.3.1. $M(IN\text{-}Dtcz)_n$ ($M = Ni(II)$, $Cu(II)$, $n = 2$). A solution of the metal salt, $MX_n \cdot xH_2O$ (0.1 g, 0.420 mmol for $M = Ni(II)$, $X = Cl$, $n = 2$, $x = 6$; 0.071 g, 0.420 mmol for $M = Cu(II)$, $X = Cl$, $n = 2$, $x = 2$) in ethanol (3 mL), was added in small portions after intervals of 10–15 min for a total of half an hour to a continuously stirred methanolic solution (6 mL) of sodium isonicotinoyldithiocarbazate (0.198 g, 0.841 mmol) prepared *in situ*. The reaction was carried out at 30–35°C. The contents of the reaction mixture were further stirred for another half an hour. The solid product obtained (light brown when M = Ni(II) and brown when M = Cu(II)) was filtered, washed with methanol and ethanol and finally with diethyl ether, and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator. Ni(IN-Dtcz)$_2$: Dec. temp.: 317°C; yield: 90%; Anal. ($C_{14}H_{12}N_6O_2S_4Ni$) Found (%): C, 34.89; H, 2.55; N, 17.21; S, 26.22; Ni, 12.22; Calcd (%): C, 34.76; H, 2.48; N, 17.38; S, 26.49; Ni, 12.15. Cu(IN-Dtcz)$_2$: Dec. temp.: 196°C; yield: 90%; Anal. ($C_{14}H_{12}N_6O_2S_4Cu$) Found (%): C, 34.01; H, 2.02; N, 17.32; S, 26.43; Cu, 12.97; Calcd (%): C, 34.42; H, 2.46; N, 17.21; S, 26.22; Cu, 13.02.

2.3.2. [M(IN-DtczH)$_n$]Cl$_n$ (M = Ni(II), Cu(II), *n* = 2). To a methanolic solution (4.45 mL) of the isonicotinoyldithiocarbazic acid (0.178 g, 0.837 mmol) prepared *in situ* was added with stirring a solution of metal salt, $MCl_n \cdot xH_2O$ (0.1 g, 0.420 mmol for M = Ni(II), $n = 2$, $x = 6$; 0.0714 g, 0.420 mmol for M = Cu(II), X = Cl, $n = 2$, $x = 2$) in ethanol (2.67 mL), in small portions (~20 mg) after successive intervals of about 10–15 min, in a total period of 1.5 h. The reaction was carried out at 30–35°C. Although the product separates out immediately or during the course of the reaction, the reaction mixture was stirred for another half an hour to ensure completion of the reaction. The solid product (light brown when M = Ni(II); dark brown when M = Cu(II)) was filtered, washed with methanol, ethanol and finally with diethyl ether, and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator. [Ni(IN-DtczH)$_2$]Cl$_2$: Dec. temp.: 270°C; yield: 85%; Anal. ($C_{14}H_{14}N_6O_2S_4Cl_2Ni$) Found (%): C, 30.45; H, 2.34; N, 15.40; S, 22.86; Ni, 10.19; Cl, 12.57; Calcd (%): C, 30.20; H, 2.51; N, 15.10; S, 23.01; Ni, 10.59; Cl, 12.76. [Cu(IN-DtczH)$_2$]Cl$_2$: Dec. temp.: 172°C; yield: 90%; Anal. ($C_{14}H_{14}N_6O_2S_4Cl_2Cu$) Found (%): C, 29.69; H, 2.45; N, 14.68; S, 22.49; Cu, 11.42; Cl, 12.21; Calcd (%): C, 29.94; H, 2.49; N, 14.97; S, 22.81; Cu, 11.32; Cl, 12.65.

2.3.3. [M(IN-DtczH-Sal)$_2$]Cl$_2$ (M = Ni(II), Cu(II)). To continuously stirred ethanolic solution of IN-DtczH-Sal (0.266 g, 0.838 mmol) was added ethanolic solution (4 mL) of metal salt $MCl_2 \cdot xH_2O$ (0.10 g, 0.420 mmol for M = Ni(II), $x = 6$; 0.072 g, 0.420 mmol for M = Cu(II), $x = 2$) in small portions after intervals of 10–15 min in a total period of half an hour. The reaction was carried out at 40–45°C. The reaction mixture was further stirred for half an hour. The solid product obtained (dirty brown when M = Ni(II); dirty green when M = Cu(II)) was filtered through Whatman filter paper no. 541, washed with methanol, ethanol and diethyl ether, and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator. [Ni(IN-DtczH-Sal)$_2$]Cl$_2$: Dec. temp.: 275°C; yield: 85%; Anal. ($C_{28}H_{22}N_6O_4S_4Cl_2Ni$) Found (%): C, 43.87; H, 2.77; N, 10.89; S, 16.62; Ni, 7.49; Cl, 9.12; Calcd (%): C, 43.96; H, 2.87; N, 10.99; S, 16.75; Ni, 7.68; Cl, 9.29. [Cu(IN-DtczH-Sal)$_2$]Cl$_2$: Dec. temp.: 220°C; yield: 88%; Anal. ($C_{28}H_{22}N_6O_4S_4Cl_2Cu$) Found (%): C, 43.56; H, 2.68;

N, 10.83; S, 16.52; Cu, 8.34; Cl, 9.18; Calcd (%): C, 43.68; H, 2.86; N, 10.92; S, 16.64; Cu, 8.26; Cl, 9.23.

2.4. *Elemental analyses and physical measurements*

Nickel and copper were determined volumetrically by EDTA titration using murexide and pyrocatechol violet as indicators, respectively. Chloride was determined volumetrically by the mercurimetric method. Carbon and hydrogen analyses were performed on an automatic Colemen-33 Analyzer while nitrogen was analyzed by Kjeldahl's method. Sulfur was determined gravimetrically as barium sulfate. Mass spectra of DMSO : ACN solution of the complex was recorded on an Agilent LCMS (6300) ion-trap mass spectrometer by electron spray ionization (ESI) source having temperature of 300°C using an EMD ion detector. Infrared (IR) spectra of isoniazid (INH), Schiff base, IN-DtczH-Sal, and all the complexes were recorded as KBr pellets on Perkin-Elmer and Nicolet 5700 FT IR Spectrophotometers from 4000 to 400 cm^{-1}. IR spectra (600–200 cm^{-1}) of the complexes were recorded as nujol mulls with cesium chloride plates as windows. IR spectra of isonicotinoyldithiocarbazic acid and sodium isonicotinoyldithiocarbazate, in methanol, were recorded with sodium chloride plates as windows (4000–400 cm^{-1}). Solution (DMSO/DMF) electronic absorption spectra of the complexes were recorded on a Cary-100 Bio UV-Vis Recording Spectrophotometer (900–200 nm) and Analytikjena Specord 200 UV-Vis Recording Spectrophotometer (1100–200 nm). Room temperature magnetic susceptibility measurements for all the complexes were made by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. Variable temperature magnetic susceptibilities of some samples were measured on a Vibrating Sample Magnetometer PAR-155 with variable temperature cryostat (model-152) using $Cu(OOCCH_3)_2 \cdot H_2O$ as calibrant. Molar conductance measurements (10^{-4} mol L^{-1} DMSO) were made at 25 ± 0.1°C using an Elico Conductivity Bridge type CM-82T [16].

3. Results and discussion

Isonicotinoyldithiocarbazic acid (IN-DtczH) (pyridine-4-carbonyldithiocarbazic acid) exists as a zwitterion (figure 1a and b), where transfer of thiol proton to pyridine nitrogen occurs because of ready availability of its lone pair as compared to that of β-nitrogen, resulting in a dipolar structure. The zwitterionic form of the dithiocarbazic acid reported [17] is obtained by the transfer of thiol proton to the β-nitrogen of the hydrazine group (figure 2).

IN-DtczH-Sal is a salicylaldehyde Schiff-base derivative of IN-DtczH and exists in zwitterionic form (figure 1).

All nickel(II) and copper(II) isonicotinoyldithiocarbazates are stable in the solid state for long periods, although it is advisable to store them over anhydrous calcium chloride. The complexes are insoluble in most common solvents, namely, cold/hot water, methanol, ethanol, acetone, chloroform, dichloromethane, and carbon tetrachloride, but have some solubility in DMSO. The complexes do not melt but decompose between 172°C and 317°C.

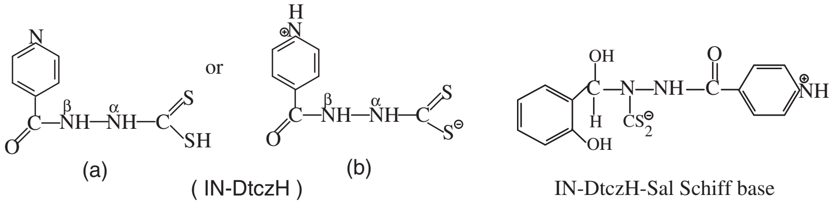


Figure 1. Zwitterionic forms of IN-DtczH and IN-DtczH-Sal.

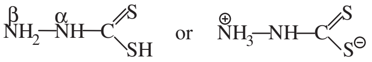


Figure 2. Zwitterionic form of dithiocarbazic acid.

Table 1. The fragmentation ions of $[Cu(IN\text{-}DtczH)_2]Cl_2$.

Fragmentation ions	m/z	Relative intensity (%)
$\{[Cu(IN\text{-}DtczH)_2]Cl_2\}_2^+$ (I)	1122	–
$[Cu(IN\text{-}Dtcz)_2]_2^+$ (II)	976	–
$[Cu_2(IN\text{-}Dtcz)_3(N_2H_2CS_2)]^{2+}$ (III)	870	–
$[Cu_2(IN\text{-}Dtcz)_2(N_2H_2CS_2)_2]^{3+}$ (IV)	764	6.25
$[Cu_2(IN\text{-}Dtcz)(N_2H_2CS_2)_3]^{4+}$ (V)	658	6.25
$[Cu_2(N_2H_2CS_2)_4]^{5+}$ (VI)	552	10.41
$[Cu_2(N_2H_2CS_2)_3(NHS)]^{5+}$ (VII)	493	43.75
$[Cu_2(N_2H_2CS_2)_2(NHS)_2]^{5+}$ (VIII)	434	100
$[Cu_2(N_2H_2CS_2)(NHS)_3]^{5+}$ (IX)	375	20.83
$2[Cu(NHS)_2]^{5+}$ (X)	157.5	6.25

3.1. *Mass spectra*

The mass spectrum of $[Cu(IN\text{-}DtczH)_2]Cl_2$ (Supplementary material – on-line) has been explained from fragments as given in table 1. Fragment ions at $m/z = 764$ (6.25%) and $m/z = 658$ (6.25%) beyond the molecular mass of the monomer may be attributed to $[Cu_2(IN\text{-}Dtcz)_2(N_2H_2CS_2)_2]^{3+}$ and $[Cu_2(IN\text{-}Dtcz)(N_2H_2CS_2)_3]^{4+}$, formed by the successive removal of 4-carbonylpyridine (C_5NH_4CO). The fragmentation of 4-carbonylpyridine of isoniazid has recently been reported by Asif Husain [18], thereby suggesting dimeric nature. However, the peak due to $m/z = 764$ is ascribed to $2M - 4HCl - 2C_5NH_4CO$ [18]. The most intense peak at $m/z = 434$ (100%) is ascribed to $[Cu_2(N_2H_2CS_2)_2(NHS)_2]^{5+}$. The spectrum displayed fragment ions corresponding to $[Cu_2(N_2H_2CS_2)_4]^{5+}$ $m/z = 552$ (10.41%) and $[Cu_2(N_2H_2CS_2)(NHS)_3]^{5+}$ $m/z = 375$ (20.83%) formed upon consequent loss of 4-carbonylpyridine (C_5NH_4CO) [18] and (NHCS) [19], respectively. Another structurally informative highly abundant ion due to $[Cu_2(N_2H_2CS_2)_3(NHS)]^{5+}$ $m/z = 493$ (43.75%) has also been observed. The fragment at $m/z = 157.5$ corresponds to $CuN_2H_2S_2$ of cation (IX).

3.2. *IR spectral studies*

A broad and intense band at 3550–3100 cm^{-1}, assignable to ν(N–H), in spectra of free IN-DtczH, IN-DtczH-Sal, and their metal complexes (table 2) as compared to sodium

Table 2. Some coordinatively diagnostic features of IR spectra (cm^{-1}) and molar conductance values, Λ_M ($\Omega^{-1}cm^2mol^{-1}$) of isonicotinoyldithiocarbazic acid, sodium isonicotinoyldithiocarbazate, salicylaldehyde Schiff base of isonicotinoyldithiocarbazic acid and their nickel(II) and copper(II) complexes.

Compound	ν(N–H)	Amide I ν(C=O)	Amide III ν(C–N)	Azomethine ν (—N — N—)	ν_a(CS)	ν(MS)	ν(MN)	ν(MO)	Λ_M
IN-DtczNa	3600–3100 b,s	1653 vs	1464 s	1053 s	1002,980 s	–	–	–	–
IN-DtczH	3300–3200 b,s	1653 vs	1410 s	1055 s	1014 s	–	–	–	–
IN-DtczH-Sal	3200–3100 b,s	1652 vs	1408 s	1064 s	1032, 999 s	–	–	–	–
Ni(IN-Dtcz)$_2$	3400–3050 b,s	1654 vs	1464 s	1064 s	1020, 1000 s	375 m	342 m	–	0
Cu(IN-Dtcz)$_2$	3400–3000 b,s	1635 vs	1467 s	1060 s	1001, 984 s	330 m	320 m	434 m	0
[Ni(IN-DtczH)$_2$]Cl$_2$	3400–3200 b,s	1655 vs	1458 s	1067 s	1020, 995 s	372 m 365 m	340 m 332 m	–	169
[Cu(IN-DtczH)$_2$]Cl$_2$	3300–3000 b,s	1635 vs	1465 s	1065 s	1030, 1015 s	325 m	316 m	435 m	168
[Ni(IN-DtczH-Sal)$_2$]Cl$_2$	3550–3250 b,s	1656 vs	1443 s	1069 s	1021, 997 s	370 m 362 m	324 m 332 m	–	170
[Cu(IN-DtczH-Sal)$_2$]Cl$_2$	3500–3200 b,s	1654 vs	1445 s	1062 s	1028, 999 s	355 m	310 m	–	165

isonicotinoyldithiocarbazate and its metal complexes, has been attributed to the existence of IN-DtczH and its Schiff-base derivative as zwitterions [20]. The $\nu(C{=}O)$ (amide I band) [21] in spectra of IN-DtczH, IN-DtczNa, and IN-DtczH-Sal has been observed at lower wavenumbers (1653–1652 cm^{-1}) (free INH shows this band at 1665 cm^{-1}). The observation of this band at lower energy can be attributed to positive charge on the nitrogen of 4-pyridine in IN-DtczH. Thus, electromeric effect comes into function and drift in electron density from the carbonyl of the amide toward the nitrogen of the pyridine ring takes place. Further decrease ($\sim$18 cm^{-1}) in this frequency is observed for $[Cu(IN\text{-}DtczH)_2]Cl_2$ and $Cu(IN\text{-}Dtcz)_2$, indicating that amide carbonyl is coordinating with metal [22]; this band is observed around 1656–1654 cm^{-1} for other complexes, showing no coordination of carbonyl (amide) to the metal. The hydrazinic  $(\overset{|}{-N}-\overset{|}{N}-)$ stretching frequencies for isoniazid, IN-DtczH, and IN-DtczNa are at 1065, 1055, and 1053 cm^{-1}, respectively [13, 23]. This band shifts $\sim$12 cm^{-1} higher energy in going from free IN-DtczH to its metal complexes and IN-DtczH-Sal suggesting bonding of the hydrazinic nitrogen to metal and to salicylaldehyde [24, 25]. Free IN-DtczH-Sal and its metal complexes exhibit $\nu(N–N)$ at 1064 and 1069–1059 cm^{-1}, respectively. The $\nu(C–N)$ of  $-\overset{\overset{O}{\|}}{C}-NH$ (amide III) is at 1420 cm^{-1} in isoniazid, while in IN-DtczH and IN-DtczH-Sal it is at 1410 and 1408 cm^{-1}, respectively. Non-observation of change in band frequency going from free IN-DtczH to IN-DtczH-Sal implies neutralization of the overall electronic effects of the whole ligand. For all metal complexes, this band is at 1445–1443 cm^{-1}, with a blue shift of $\sim$32–35 cm^{-1}. The spectra of our dithiocarbazate complexes exhibit strong absorption at 1030–1000 cm^{-1}. In every case this absorption is either split into two bands or has well-defined shoulders, further supporting unidentate sulfur coordination with NS/ONS [26, 27]. The appearance of additional bands at 435–310 cm^{-1}, in the complexes (table 2), as compared to free IN-DtczH, IN-DtczNa, and IN-DtczH-Sal reveals the formation of M–S, M–N, and M–O bonds [24, 25, 28].

3.3. *Molar conductance studies*

The molar conductances of DMSO solutions of the zwitterionic complexes, $[M(IN\text{-}DtczH)_2]Cl_2$ and $[M(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$ ($M = Ni(II)$, $Cu(II)$) are 165–170 $\Omega^{-1}\,cm^2\,mol^{-1}$ (table 2), corresponding to 1 : 2 electrolytic behavior [29]. $Ni(IN\text{-}Dtcz)_2$ and $Cu(IN\text{-}Dtcz)_2$ are non-electrolytes.

3.4. *Magnetic susceptibility studies*

The room temperature magnetic moment of $Ni(IN\text{-}Dtcz)_2$ is zero, exhibiting diamagnetic behavior, and suggesting square planar $[NiN_2S_2]$ geometry around nickel(II). $[Ni(IN\text{-}DtczH)_2]Cl_2$ and $[Ni(IN\text{-}DtczH\text{-}Sal)_2]Cl_2$ have room temperature magnetic moments of 2.6 and 2.1 B.M., respectively, which decrease with the decreasing temperature (1.45 and 1.52 B.M. at 80 K, respectively) (figure 3). The magnetic properties of these complexes can be attributed to the presence of configurational square planar, ^1A_g $(S = 0) \rightleftharpoons$ tetrahedral, $^3T_1$ $(S = 1)$ equilibrium. This behavior is unusual in that no nickel(II) dithiocarbazate has been reported to exhibit this square planar $\rightleftharpoons$ tetrahedral

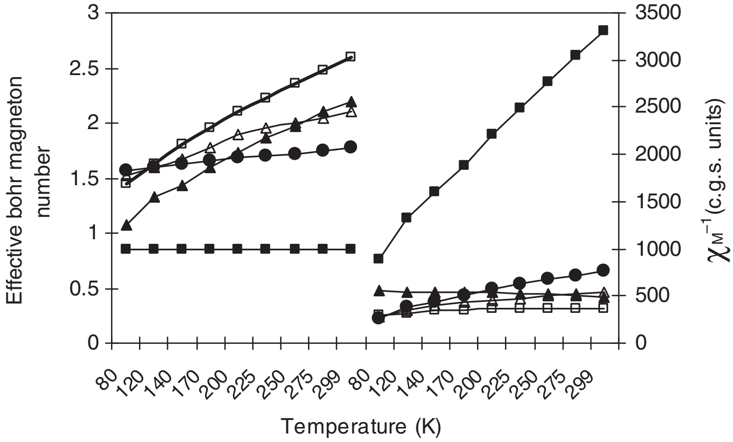
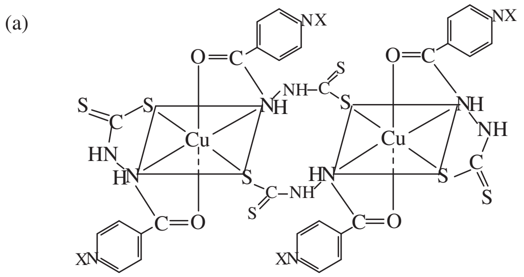


Figure 3. Variation of effective Bohr magneton and χ_M^{-1} of [Ni(IN-DtczH)$_2$]Cl$_2$ (–□–), [Ni(IN-DtczH-Sal)$_2$]Cl$_2$ (–Δ–), Cu(IN-Dtcz)$_2$ (–■–), [Cu(IN-DtczH)$_2$]Cl$_2$ (–▲–) and [Cu(IN-DtczH-Sal)$_2$]Cl$_2$ (–•–) with temperature.

equilibrium, although such phenomena are well-known for other bis(*o*-hydroxynaphthaldiminato)nickel(II) and bis(*N*-sec-alkylsalicylaldiminato)nickel(II) complexes [30]. This is quite surprising as Ni(IN-Dtcz)$_2$ with similar [NiN$_2$S$_2$] chromophore exhibits pure square-planar geometry. This change in configurational behavior may be influenced by the change in nature of the ligands, zwitterionic IN-DtczH, and IN-DtczH-Sal and the presence of anions in the secondary coordination sphere of the complexes. Both these factors lead to greater steric interactions and stabilize tetrahedral geometry at room temperature. Using the relationship, $\mu_{\mathrm{exp}}^2 = x\,\mu_{\mathrm{sp}}^2 + (1-x)\,\mu_{\mathrm{Td}}^2$ (μ_{exp} is the experimental effective Bohr magneton number, μ_{sp} and μ_{Td} are the effective Bohr magneton numbers for the pure square planar and tetrahedral geometries and x is the mole fraction for the square-planar complex) and with $\mu_{\mathrm{sp}} = 0.0$ and $\mu_{\mathrm{Td}} = 3.6$ for pure square planar and tetrahedral geometries around nickel(II), the room temperature percentage of tetrahedral geometry for the complexes are 52% and 34%, respectively; the low-temperature percentages are 16% and 17.8%, respectively. In both cases, the percentage of square planar geometry at low temperature (80 K) increases (84% and 82%, respectively) but in neither is the pure square planar geometry attained.

For Cu(IN-Dtcz)$_2$ and [Cu(IN-DtczH)$_2$]Cl$_2$, with [CuO$_2$N$_2$S$_2$] chromophore, calculated room temperature μ_{eff} values are 0.85 and 2.20 B.M., respectively. The magnetic behavior for the former complex is unusual since the μ_{eff} value is less than those for magnetically dilute copper(II) complexes ($\mu_{\mathrm{eff}}^{\mathrm{S.O.}}$ value for one unpaired electron = 1.73 B.M.) [31]. The observed value, however, falls in the range of values reported for dinuclear or polynuclear copper(II) dithiocarbazate complexes in which spin–spin interaction through bridging ligands has been proposed [32, 33]. The unusual room temperature magnetic behavior for Cu(IN-Dtcz)$_2$ as well as the room temperature magnetic moment of [Cu(IN-DtczH)$_2$]Cl$_2$ prompted us to extend the magnetic susceptibility measurements to liquid nitrogen temperature. For Cu(IN-Dtcz)$_2$ the magnetic moment is invariant with temperature (299–80 K). Although this is surprising, it can be assumed that stronger antiferromagnetic interactions through bridging ligands, due to greater covalency than its zwitterionic analog, has reached the maximum

(a)



X = Nil for $Cu(IN\text{-}Dtcz)_2$ and X = H^+----Cl for $[Cu(IN\text{-}DtczH)_2]Cl_2$

(b)

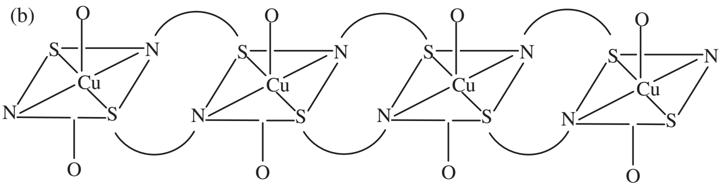


Figure 4. Proposed (a) dimeric and (b) polymeric structures for $Cu(IN\text{-}Dtcz)_2$ and $[Cu(IN\text{-}DtczH)_2]Cl_2$.

even at room temperature. This will lead to a reduction in indirect exchange interaction and a consequent decrease in antiferromagnetic interactions, since indirect exchange takes place largely through interaction of the delocalized pi-bonding framework of the bridging isonicotinoyldithiocarbazates with d-orbitals of the metal. For $[Cu(IN\text{-}DtczH)_2]Cl_2$, μ_{eff} values decrease with the decreasing temperature (1.08 B.M. at 80 K) (figure 3). Insolubility in water and common organic solvents with the low value of room temperature effective Bohr magneton for the former and the temperature dependence of magnetic moments for the latter, which are characteristics of magnetically exchange-coupled (antiferromagnetic) pairs, indicate that the complexes may be dimeric or polymeric [32] (figure 4).

Variation of magnetic susceptibility with temperature for such systems is given by

$$\chi_{Cu} = \frac{Ng^{-2}\beta^2}{3kT}\left(1 + \frac{1}{3}e^{-2J/kT}\right)^{-1} + N\alpha \tag{1}$$

based on Bleaney and Bower's model [34], where χ_{Cu} is the average magnetic susceptibility per gram atom of copper(II), $-2J$ is the spin exchange parameter and gives the difference in energies of the diamagnetic (spin-singlet) state and paramagnetic (spin-triplet) state, k is the Boltzmann constant (=0.69503 $cm^{-1}\,deg^{-1}$), $N\alpha$ is the temperature-independent paramagnetism (60×10^{-6} c.g.s. mol^{-1}), T is the absolute temperature, N is Avogadro's number, β is the Bohr magneton (0.9273×10^{-20} erg guass^{-1}), $N\beta^2/k = 0.3753$, and g is the average g-value (=2.2 [32, 35]). Using this equation for χ_{Cu}, the value of $2J$ may be obtained by the graphical method described by Herring *et al.* [36]. In this method after putting $3 + e^{-2J/kT}$ equal to F, equation (1) is rearranged as:

$$F = 3 + e^{-2J/kT} = \frac{Ng^{-2}\beta^2}{kT(\chi_{Cu}^{-}N\alpha)} \tag{2}$$

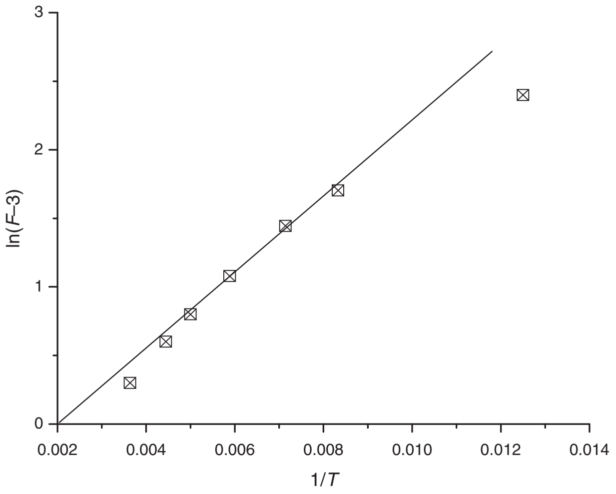


Figure 5. Plot of ln($F-3$) *vs.* $1/T$ for [Cu(IN-DtczH)$_2$]Cl$_2$.

$$\ln(F-3)=\left|\frac{2J}{kT}\right|=\ln\left[\frac{Ng^{-2}\beta^2}{kT(\chi_{\mathrm{Cu}}^{-}N\alpha)}-3\right] \tag{3}$$

A plot of $\ln(F-3)$ *versus* $1/T$ should give a straight line passing through the origin with slope $2J/k$, the measurement of which will yield the value of $2J$.

For [Cu(IN-DtczH)$_2$]Cl$_2$, a straight line for the $\ln(F-3)$ *versus* $1/T$ plot (figure 5) was obtained and its slope $= 2J/k$ was measured. Using the value of $k = 0.69503\,\mathrm{cm}^{-1}\,\mathrm{deg}^{-1}$, $2J$ was evaluated to be $202\,\mathrm{cm}^{-1}$. This value is comparable to that for earlier reported copper(II) dithiocarbazate complexes [32]. The $2J$ value for Cu(IN-Dtcz)$_2$ could not be evaluated because the slope was negative due to non-variation of its magnetic moment value with temperature.

The room temperature μ_{eff} value of [Cu(IN-DtczH-Sal)$_2$]Cl$_2$ is 1.77 B.M. corresponding to one unpaired electron. Very small decrease in μ_{eff} value of 0.2 B.M. (1.57 B.M. at 80 K) may be attributed to weak antiferromagnetic interactions due to the ligand bridging the two square-planar units in a dimeric structure (figure 6).

3.5. *Electronic absorption spectral studies*

In the DMSO electronic absorption spectrum of Ni(IN-Dtcz)$_2$, the lowest energy band at 689 nm is assigned to parity-forbidden $^1B_{1g} \leftarrow {}^1A_g$ ($x^2{-}y^2 \rightarrow xy$) transition and the higher energy band at 565 nm to $^1B_{3g} \leftarrow {}^1A_g$ ($xz \rightarrow xy$) [25]. The shoulder at 465 nm and a strong band at 368 nm are assigned to metal-to-ligand charge transfer $^1B_{2u} \leftarrow {}^1A_g$ [3d$_{xz} \rightarrow$ L(π*)] and $^1B_{3u} \leftarrow {}^1A_g$ [3d$_{yz} \rightarrow$ L(π*)] transitions, respectively [37]. Electronic absorption spectra (DMSO) of nickel(II) dithiocarbazates, namely [Ni(IN-DtczH)$_2$]Cl$_2$ and [Ni(IN-DtczH-Sal)$_2$]Cl$_2$, show five absorptions, (i) weak band at 1111–1100 nm; (ii) broad band at 699–625 nm; (iii) medium intensity band at 566–555 nm; (iv) strong band at 440–417 nm; and (v) very strong band at 346–333 nm. Because of the existence of planar-tetrahedral equilibrium from magnetic behavior, electronic transitions seem to

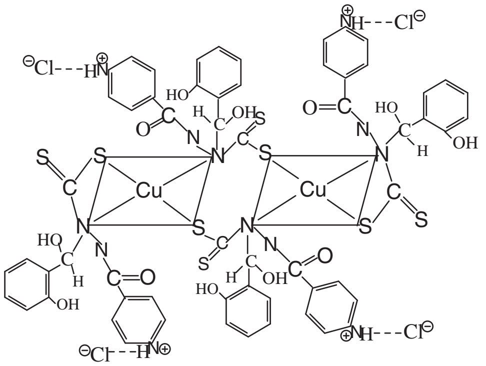


Figure 6. Proposed dimeric structure for [Cu(IN-DtczH-Sal)$_2$]Cl$_2$.

be characteristic of tetrahedral as well as square planar geometry around nickel(II). Therefore, the observed absorptions may be described in the tetrahedral and square planar geometry of nickel(II) as: (i) $^3A_2 \leftarrow {}^3T_1$; (ii) $^3T_1(\mathrm{P}) \leftarrow {}^3T_1(\mathrm{F})$, $^1B_{1g} \leftarrow {}^1A_g$ $(x^2-y^2 \rightarrow xy)$; (iii) $^1B_{3g} \leftarrow {}^1A_g$ $(xz \rightarrow xy)$; (iv) $^1B_{2u} \leftarrow {}^1A_g$ $[3\mathrm{d}_{xz} \rightarrow \mathrm{L}(\pi^*)]$; and (v) $^1B_{3u} \leftarrow {}^1A_g$ $[3\mathrm{d}_{yz} \rightarrow \mathrm{L}(\pi^*)]$. Observation of band (i) in the near IR region due to tetrahedral geometry as well as the broadness of band (ii) due to overlapping of transitions of the square planar and tetrahedral geometries and appearance of high-energy bands (iv) and (v) of square planar geometry, complement the room temperature μ_{eff} values and their temperature-dependent behavior. Such unusual behavior has also recently been reported for cobalt(II) dithiocarbazates with d^7 configuration [16, 38]. Observation of separate bands in electronic absorption spectra arises because interconversion time of square planar geometry to tetrahedral geometry is large compared to the time required for an electronic transition to take place (10^{-15} s). The electronic spectra of iron(III) dithiocarbamate complexes, in which spin-free–spin-paired equilibrium exists consists of the superposition of separate peaks which characterize each spin state rather than an "averaged spectrum" [39].

The spectral assignments are justified as binding of solvent during solution electronic absorption spectral measurements and may change the geometry from square planar or tetrahedral to octahedral. But the solid-state temperature-dependent behavior of magnetic moments as well as the conducting (1 : 2) electrolytic nature of both nickel(II) complexes rules out the existence of octahedral structures through solid–solvent interactions.

Cu(IN-Dtcz)$_2$ and [Cu(IN-DtczH)$_2$]Cl$_2$ show two separate bands at 835–645 nm and a shoulder at 400–390 nm in their electronic absorption spectra in DMSO. The lower energy band splits and appears as a low-intensity band at 835 nm and as a high-intensity band at 660–645 nm. These are considered to contain bands due to $\mathrm{d}_{xy} \rightarrow \mathrm{d}_{x2-y2}$ and $(\mathrm{d}_{xz},\ \mathrm{d}_{yz}) \rightarrow \mathrm{d}_{x^2-y^2}$ electronic transitions for copper(II) ion in tetragonally distorted octahedral environment. The band II which appears as a shoulder around 400–390 nm is assigned to L→M charge transfer $2\mathrm{p}_\pi \rightarrow (\mathrm{d}_{x^2-y^2})$. [Cu(IN-DtczH-Sal)$_2$]Cl$_2$ exhibits four bands in its DMSO solution electronic absorption spectrum. High-intensity bands at 335 and 305 nm are assigned to intraligand absorptions n→π^* and π→π^*. A band at 730 nm is assigned to a d–d transition. Additionally a band of high intensity at

455–400 nm, which is unsymmetrical, has been assigned to S → Cu^{II} charge transfer. The presence of a S → Cu (LMCT) band in the electronic absorption spectrum of this complex further supports bonding of ligand to the metal ion *via* sulfur. The occurrence of S → Cu (LMCT) band and the position of the d–d band are similar to those of other square-planar copper(II) complexes of related ligands, whose structures have been determined by X-ray diffraction [40, 41].

References

[1] M.A. Ali, H.J.H. Abu Bakar, A.H. Mirza, S.J. Smith, L.R. Gahan, P.V. Bernhardt. *Polyhedron*, **27**, 71 (2008).
[2] M.A. Ali, A.H. Mirza, F.H. Bujang, M.H.S.A. Hamid, P.V. Bernhardt. *Polyhedron*, **25**, 3245 (2006).
[3] J.T. Makode, A.S. Aswar. *Ind. J. Chem.*, **43A**, 2120 (2004).
[4] S.Y. Ucan, B. Mercimek. *Synth. React. Inorg. Met-Org. Nano Met. Chem.*, **35**, 197 (2005).
[5] M.A. Ali, S.E. Livingstone. *Coord. Chem. Rev.*, **13**, 101 (1974).
[6] M.R. Maurya, N. Bharti, F. Naqvi, A. Azam. *Bioinorg. Med. Chem. Lett.*, **10**, 2243 (2000).
[7] Shailendra, N. Bharti, F. Naqvi, A. Azam. *Helv. Chim. Acta*, **85**, 2713 (2002).
[8] M.A. Ali, M.C. Haroon, M. Nazimuddin, S.M. Majumdar, Mahbub Ul Haque, M.T.H. Tarafder, M.A. Khair. *Transition Met. Chem. (London)*, **17**, 133 (1992).
[9] S. Kalia, K. Lumba. *Dithiocarbazates and their Transition Metal Complexes*, LAP Lambert Academic Publishers, Germany (2010).
[10] M. Das, S.E. Livingstone. *Br. J. Cancer*, **37**, 101 (1978).
[11] M.T.H. Tarafder, K.-B. Chew, K.A. Crouse, A.M. Ali, B.M. Yamin, H.-K. Fun. *Polyhedron*, **21**, 2683 (2002).
[12] K.A. Crouse, K.-B. Chew, M.T.H. Tarafder, A. Kasbollah, A.M. Ali, B.M. Yamin, H.-K. Fun. *Polyhedron*, **23**, 161 (2004).
[13] M.E. Hossain, M.N. Alam, M.A. Ali, M. Nazimuddin, F.E. Smith, R.C. Hynes. *Polyhedron*, **15**, 973 (1996).
[14] M.E. Hossain, M.N. Alam, J. Begum, M.A. Akbar, M. Nazimuddin, F.E. Smith, R.C. Hynes. *Inorg. Chim. Acta*, **249**, 207 (1996).
[15] J. Bernstein, W.A. Lott, B.A. Steinberg, H.L. Yale. *Ann. Rev. Tuberc.*, **76**, 568 (1952).
[16] S.B. Kalia, K. Lumba, G. Kaushal, M. Sharma. *Ind. J. Chem.*, **46A**, 1233 (2007).
[17] G. Gattow, W. Behrendt. In *Topics in Sulfur Chemistry*, A. Senning (Ed.), Vol. 2, p. 97, Thieme-Verlag, Stuttgart (1977).
[18] A. Husain. *Acta Poloniae Pharmaceutica – Drug Res.*, **66**, 513 (2009).
[19] B. Singh, T.B. Singh. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 583 (2000).
[20] M.A. Ali, R.N. Bose. *Polyhedron*, **3**, 517 (1984).
[21] J. Mohan. *Organic Spectroscopy – Principles and Application* (2001).
[22] R.K. Agarwal, H. Agarwal, K. Prasad. *J. Ind. Chem. Soc.*, **73**, 605 (1996).
[23] S.K. Singh, S.B. Singh, D.K. Singh, V.B. Chauhan. *Ind. J. Chem.*, **42A**, 2767 (2003).
[24] P. Tripathi, A. Pal, V. Jancik, A.K. Pandey, J. Singh, N.K. Singh. *Polyhedron*, **26**, 2597 (2007).
[25] T.B.S.A. Ravoof, K.A. Crouse, M.I.M. Tahir, A.R. Cowley, M.A. Ali. *Polyhedron*, **26**, 1159 (2007).
[26] K.A. Crouse, K-B. Chew, M.T.H. Tarafder, A. Kasbollah, M.A. Ali, B.M. Yamin, H-K. Fun. *Polyhedron*, **23**, 161 (2004).
[27] M.A. Ali, A.H. Mirza, M. Nazimuddin, H. Rahman, R.J. Butcher. *Transition Met. Chem.*, **27**, 268 (2002).
[28] M.A. Ali, A.H. Mirza, M.S.H. Khan, R.J. Butcher, M.T.H. Tarafder, T.B. Keat, A.M. Ali. *Transition Met. Chem.*, **27**, 262 (2002).
[29] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[30] R.L. Dutta, A. Syamal. *Elements of Magnetochemistry*, S. Chand & Co., New Delhi (1982).
[31] B.N. Figgis, J. Lewis. *Prog. Inorg. Chem.*, **6**, 37 (1964).
[32] M.A. Ali, S.E. Livingstone, D.J. Phillips. *Inorg. Chim. Acta*, **7**, 179, 531 (1973).
[33] M.A.S. Monshi, N.M.A. Salem. *J. Chem. Soc. Pak.*, **18**, 155 (1996).
[34] B. Bleaney, K.D. Bowers. *Proc. R. Soc., London*, **214A**, 451 (1952).
[35] M.A. Ali, A.H. Mirza, M.S.H. Khan, R.J. Butcher, M.T.H. Tarafder, T.B. Keat, A.M.A. Ali. *Transition Met. Chem.*, **27**, 262 (2002).
[36] R.C. Thompson, F.G. Herring, B. Landa, C.F. Schwerdtfegr. *J. Chem. Soc. A*, 528 (1971).

[37] O. Siimann, J. Fresco. *J. Am. Chem. Soc.*, **92**, 2652 (1970).
[38] B.S. Manhas, B.C. Verma, S.B. Kalia. *Polyhedron*, **14**, 3549 (1995).
[39] R.L. Martin, A.H. White. *Transition Met. Chem.*, **4**, 113 (1968).
[40] M.A. Ali, A.H. Mirza, R.J. Butcher. *Polyhedron*, **20**, 1037 (2001).
[41] M.A. Ali, K.K. Dey, M. Nazimuddin, R.J. Butcher, F.E. Smith, J.P. Jasinski, J.M. Jasinski. *Polyhedron*, **15**, 3331 (1996).