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Anagostic interactions, revisiting the crystal structure of nickel dithiocarbamate complex and its antibacterial and antifungal studies

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ABSTRACT

The synthesis of Ni(dtc)₂ [dtc = diethyldithiocarbamate] has been achieved by the interaction of NiL(ClO₄)₂ with sodium diethyldithiocarbamate. Although single crystal structure of this complex was already reported (R = 10.6%), we were able to refine crystal structure up to R = 2.99%. We also observed rare C-H···Ni anagostic interactions generally exhibited by d⁸ complexes which were overlooked previously. To investigate the structure of Ni(dtc)₂ in solution, variable temperature NMR spectra in solution have also been recorded between 25 and -50 °C. Ni(dtc)₂ was also tested for antibacterial and antifungal activities. It showed higher activity against the bacteria and fungi than the known antibiotics.

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1. Introduction

Dithiocarbamate based coordination complexes have been thoroughly studied because of their ability to coordinate many common metal ions in different binding modes [1]. They have been shown to possess a broad spectrum of biological activities such as fungicidal [2,3] and bactericidal [4,5]. The antibacterial and antifungal activities of dithiocarbamates were reported to arise by the reaction with HS-groups of the physiologically important enzymes by transferring the alkyl group of the dithioester to the HS-function of the enzyme [5]. All dithiocarbamates contain the characteristic disulfur moiety that binds metal ions in monodentate or bidentate fashion. The nitrogen may be functionalized in various ways to modify the physico-chemical properties of the ensuing metal complex, particularly its solubility and lipophilicity [6]. The dithiocarbamate core, $M-S_2CNR_2$ (M = Metal, R = Alkyl) could prove to be of great synthetic utility since a wide variety of organic substituents can be incorporated in this stable bidentate ligand system. It gives rise to the chemical 'fine-tuning' of the biological properties of the complex by variation of the substituent R in M–S₂CNR₂ [7].

Recently, we have explored the chemistry of $[Ni(L)][CoCl_4]$ [where L = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo(3.3.1)nonane] complex [8]. As an extension of our previous findings, we report in this paper the reaction of NiL(ClO₄)₂ with sodium

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diethyldithiocarbamate which resulted in a ligand transfer reaction. The resulting compound was characterized as Ni(dtc)₂ by single crystal X-ray diffraction and other spectroscopic studies and evaluated for antibacterial and antimicrobial properties.

2. Experimental

2.1. Materials and methods

Reagent grade sample of NiCl₂.6H₂O, sodium diethyldithiocarbamate (Fluka), ethylenediamine (Acros), Ammonia solution (25%) and formaldehyde (S.D. Fine) were used as received and all experiments were carried out in an open atmosphere. All solvents were purchased from Merck India and used after purification. Elemental analyses (C, H, N and S) were carried out with a Carlo Erba EA-1108 analyzer. IR spectra (4000–400 cm⁻¹) were recorded with a RXI FT-IR spectrometer as KBr disc. The NMR spectra were recorded with a BRUKER AV-400 in CDCl₃.*Caution!* Although our samples never exploded during handling, perchlorate metal complexes are potentially explosive: they should be handled with care.

2.2. Synthesis

 $[Ni(L)(ClO_4)_2]$ [where L = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo(3.3.1)nonane] was synthesized as reported earlier [9]. To an aqueous solution of $[Ni(L)(ClO_4)_2]$ (5 mM, 2.36 g) an ethanolic solution of sodium diethyldithiocarbamate (10 mM, 1.69 g) were added dropwise with continuous stirring. The solution





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Scheme 1. Synthesis of Ni(dtc)₂.

immediately turned green followed by the formation of dark green precipitate which was filtered and washed several times with distilled water and dried in vacuo. The resulting compound was characterized as Ni(dtc)₂ (Scheme 1) by spectroscopic studies. In a competing process, the Ni(L)(ClO₄)₂ complex undergoes demetalation immediately due to sodium diethyldithiocarbamate to yield nickel(II) bis(*N*,*N*-diethyldithiocarbamate). X-ray quality crystals of Ni(dtc)₂ were grown by slow evaporation of chloroform solution at room temperature. Yield: 58%. M.p. 537 K. ¹H NMR (CDCl₃; 400 MHz, d ppm): 1.23 (*t*, *J* = 7.2 Hz, 12H, CH₃), 3.6 (*q*, *J* = 14.4 Hz, 8H, CH₂). IR (ν cm⁻¹, KBr): ν (CSS) 993, ν (C···N) 1517; *Anal.* Calc. for C₁₀H₂₀N₂NiS₄: C, 33.83; H, 5.68; N, 7.89; S, 36.06; Ni, 16.54. Found: C, 33.40; H, 5.45; N, 7.76; S, 35.95; Ni, 16.65%.

2.3. Crystal structure determination

Single-crystal X-ray structural study was performed on a CCD Bruker SMART APEX Diffractometer equipped with an Oxford Instrument low-temperature attachment. Data were collected at 100(2) K using graphite monochromated Mo K α radiation (λ_{α}) 0.71073 Å. The frames were indexed, integrated, and scaled using the smart and saint software package [10] and the data were corrected for absorption using the sadabs [11] program. The structure was solved by direct method and refined using the shelx-97 [12] suite of programs, while additional crystallographic calculations were performed by the program PLATON [13]. Figures were drawn using ORTEP-3.2 [14a] and MERCURY-2.3 [14b]. The hydrogen atoms were included at geometrically calculated positions in the final stages of the refinement and were refined according to the "riding model". All non-hydrogen atoms were refined with anisotropic thermal parameters.

3. Results and discussion

3.1. Crystal structure description of [Ni(dtc)₂]

The molecular structure of the $[Ni(dtc)_2]$ complex along with the atomic numbering scheme is shown in Fig. 1, Crystallographic



Fig. 1. Molecular structure of Ni(dtc)₂ depicting the Ni…H and S…H interactions. (MERCURY software has been used for the drawing, bond lengths have been measured in angstrom; only the atoms involving in the interactions are labeled for clarity).

Table 1

Crystallographic data	for nickel(II)	bis(N.N-diethyld	ithiocarbamate).

Empirical formula	C ₁₀ H ₂₀ N ₂ NiS ₄
Formula weight	355.25
Melting point (K)	537
Crystal system	monoclinic
Space group	$P2_1/c$
T (K)	298
a (Å)	6.0080 (12)
b (Å)	11.441 (2)
<i>c</i> (Å)	11.543 (2)
β(°)	95.98 (3)
V (Å ³)	789.1 (3)
Ζ	2
$ ho_{\rm calc} ({ m g}{ m cm}^{-3})$	1.495
$\mu (\mathrm{mm}^{-1})$	1.74
F(0 0 0)	372
Crystal size (mm)	$0.25 \times 0.12 \times 0.09$
θ Range for data collection (°)	2.2–25.5
Index ranges	$-7 \le h \le 6; -13 \le k \le 13;$
	$-9 \le l \le 13$
Number of reflections collected	4127
Number of independent reflections	1460 (0.038)
(K_{int})	1201
Number of observed $[I > 2\sigma(I)]$ reflections	1361
Number of data/restraints/parameters	1460/0/81
Goodness-of-fit (GOF) on F^2	1.14
$R[F^2 > 2\sigma(F^2)]$	0.029
$wR(F^2)$	0.075
$\Delta ho_{ m max}$ and $\Delta ho_{ m min}$ (e Å $^{-3}$)	0.45 and -0.45
Data completeness	0.993

Table	2
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Selected bond lengths (Å) and angles (°).

Bond lengths				
Ni1-S2 ⁱ	2.2026 (8)	C1-H1B	0.9700	
Ni1-S2	2.2026 (8)	C2-H2A	0.9600	
Ni1-S1	2.2042 (6)	C2-H2B	0.9600	
Ni1–S1 ⁱ	2.2042 (6)	C2-H2C	0.9600	
S1-C5	1.719 (2)	C3-C4	1.515 (3)	
S2-C5	1.724 (2)	C3–H3A	0.9700	
N1-C5	1.317 (3)	C3-H3B	0.9700	
N1-C1	1.467 (3)	C4–H4A	0.9600	
N1-C3	1.478 (3)	C4–H4B	0.9600	
C1-C2	1.525 (3)	C4-H4C	0.9600	
C1-H1A	0.9700			
Bond angles				
S2 ⁱ -Ni1-S2	180.0	H2A-C2-H2B	109.5	
S2 ⁱ -Ni1-S1	100.57 (2)	C1-C2-H2C	109.5	
S2-Ni1-S1	79.43 (2)	H2A-C2-H2C	109.5	
S2 ⁱ -Ni1-S1 ⁱ	79.43 (2)	H2B-C2-H2C	109.5	
S2-Ni1-S1 ⁱ	100.57 (2)	N1-C3-C4	111.62 (17)	
S1-Ni1-S1 ⁱ	180.0	N1-C3-H3A	109.3	
C5-S1-Ni1	85.38 (7)	C4-C3-H3A	109.3	
C5-S2-Ni1	85.31 (7)	N1-C3-H3B	109.3	
C5-N1-C1	121.19 (17)	C4-C3-H3B	109.3	
C5-N1-C3	121.42 (18)	НЗА-СЗ-НЗВ	108.0	
C1-N1-C3	117.31 (16)	C3-C4-H4A	109.5	
N1-C1-C2	111.15 (18)	C3-C4-H4B	109.5	
N1-C1-H1A	109.4	H4A-C4-H4B	109.5	
C2-C1-H1A	109.4	C3-C4-H4C	109.5	
N1-C1-H1B	109.4	H4A-C4-H4C	109.5	
C2-C1-H1B	109.4	H4B-C4-H4C	109.5	
H1A-C1-H1B	108.0	N1-C5-S1	124.82 (16)	
C1-C2-H2A	109.5	N1-C5-S2	125.44 (16)	
C1-C2-H2B	109.5	S1-C5-S2	109.74 (11)	

Symmetry code: (i) -x + 1, -y + 1, -z + 1.

data, selected bond lengths and bond angles are given in Tables 1 and 2. $[Ni(dtc)_2]$ was crystallized in monoclinic system with $P2_1/c$ space group in body centered lattice. The unit cell contains two

units of Ni(dtc)₂ (Fig. 2). The unit cell parameters were found to be a = 6.0080 (12), b = 11.441 (2), c = 11.543 (2) Å, $\beta = 95.98 (3)^{\circ}$ which are considerably different from that reported by Bonamico et al. [15], Selvaraju and Panchanatheswaran [16] Khan et al. [17] and Hogarth et al. [1]. The major change takes place in the refinement factor, R which is improved from 10.6% to 2.99%. Two independent dithiocarbamate moiety coordinate to the nickel atom to form the complex. The nickel atom is four-coordinated with two sulfur atoms of each diethyldithiocarbamate ligand giving rise to a square planar arrangement. The bond angle of four-membered chelate rings around the Ni(II) is 109.75° which is in close proximity with a square planar Ni(II) ion. The near equality of the two Ni-S and two C–S distances confirm the isobidentate coordination of the dithiocarbamate group. The difference between the Ni-S1 and Ni-S2 bond lengths is only 0.001 (6). For comparison, the corresponding differences were 0.012 in the previous determination. The accuracy in the C1–N bond length of 1.317 (3) is an order of magnitude higher than that reported earlier $[1.33 (10)/\sim]$. The Ni atom lies on a centre of symmetry and participates in two short symmetrically related Ni…H contacts of 2.665 Å with H3A atoms attached to C3 [symmetry code: (i) -x + 1, -y + 1, -z + 1]. The torsion angles C1-N1-C5-S2 [-5.2 (3)°], C1-N1-C5-S1 [174.6 (2)°], C3-N1-C5-S1 [-2.1 (3)°] and C3-N1-C5-S2 [178.0 (2)°] confirm the near planarity of the S₂CNR₂ moiety.

In an attempt to understand the supramolecular arrangement of the Ni $(dtc)_2$ molecules, the packing and hydrogen bonding interactions between the molecules were analyzed in detail. The packing and Ni \cdots H bonding interactions viewed along the a-axis are shown in Fig. 3. In addition to this, the hydrogen H3A of the methyl group is also involved in an S \cdots H–C interaction propagating into a three dimensional hydrogen bonded network (Figs. 4–7).

Generally, there are three forms of C-H...M interactions including (i) hydrogen bond, (ii) agostic and (iii) anagostic [18]. Hydrogen bonds (i) are 3-center-4-electron interactions with an almost linear geometry accompanied by a downfield ¹H NMR shift of the participating H atom. Agostic M. H-C interactions are usually referred to as a 3-centre-2-electron interaction, resulting in a pronounced highfield chemical shift of the corresponding H atom and characterized by relatively short M···H distances of \approx 1.8–2.2 Å and C– H···M bond angles of \approx 90–130°. Such interactions are often found in d⁶ complexes. Anagostic interactions [18–25] occurring (Fig. 3) in square planar d⁸ systems are of broad general interest due to possible implications for the mechanism of C-H activation [26-27]. Anagostic interactions are characterized by relatively long M···H distances (\approx 2.3–2.9 Å) and large M···H–C bond angles $(\approx 110-170^{\circ})$. In the present case M···H distances is 2.665 Å and $M \cdots H-C$ bond angle is 142.4°. They are in between the hydrogen bonds and agostic interactions, with characteristic downfield shifts of the anagostic protons. Although the origin of these interactions is still under debate it may involve donation of filled d_z^2 or $d_{xz/yz}$ orbitals of the metal center into the C–H σ^* orbital [28]. The nature of the anagostic M···H–C interaction in a variety of square planar d⁸ compounds was recently addressed theoretically by Zhang et al. [29].

The methylene group to which the metal is attached through anagostic-type bond, can be envisaged as a dative bond from the X–H σ bonding orbital to the empty 4s orbital of the metal, and a back-donation from the valence electron pairs of the metal into the X–H σ^* antibonding orbital of the neutral species.

A specific interaction C–H···S (Figs. 4–6) apparently takes place between the hydrogen atom of the second methylene group and the thioureide sulfur. The existence of specific interactions C– H···S is manifested by anomalous downfield shift of the signal from the corresponding proton. This observed shift may be due to specific interaction C–H···S, or it may be due to the influence of anisotropy of the –CSS group [30], the interatomic S···H distance



Fig. 2. Unit cell of Ni(dtc)₂. Molecules have been shown as ORTEP diagram with 50% thermal ellipsoids. All hydrogen atoms have been omitted for clarity.



Fig. 3. Two dimensional packing diagram depicting the Ni…H interactions bonded network along *a*-axis.

corresponding to the equilibrium geometry was found to be 3.0 Å, equal to the sum of the van der Waals radii of the hydrogen and sulfur atoms [31] and $S \cdots H-C$ bond angle was found to be 171.7°.

3.2. ¹H NMR studies

To investigate the structure of Ni(dtc)₂ in solution, ¹H NMR spectra of the complex was recorded in CDCl₃ solution at variable temperatures ranging from 25 °C to -50 °C (Fig. 8). All post acqui-

sition data processing was performed with the MestReC NMR software package [32]. The ¹H NMR spectrum at room temperature shows only a single set of signals, suggesting that the two ligands are equivalent in solution. In the ¹H NMR spectrum of Ni(dtc)₂ the $-CH_2-$ protons were observed at 3.54 ppm while in case of ligand it was reported at 4.02 ppm. Interestingly, upon cooling the sample to -50 °C the signals start to broaden. Similar observations have also been reported for C-H···M interactions in d⁸ square-planar complexes of Pd(II) [33], Pt(II) [34] and Ni(II) [27,35] have been reported recently.



Fig. 4. Two dimensional packing diagram depicting the S···H interactions bonded network along *a*-axis. Hydrogen atoms except those involving in interaction have been omitted for clarity. Ni – green, S – yellow, N – sky blue, C – dark grey, H – light grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. 1D packing diagram depicting the S…H interactions bonded network along *b*-axis.



Fig. 6. 3D packing diagram depicting the S...H interactions bonded network along *c*-axis.



Fig. 7. 3D packing diagram of the three dimensional coordination network showing the staggered arrangement of adjacent sheets depicting the Ni…H and S…H interactions.

4. Biological activity

The antibacterial and antifungal activity of $Ni(dtc)_2$ was determined against three bacterial strains (*Escherichia coli, Bacillus*)

thuringiensiso and Pseudomonas aeruginosa) and three fungal strains (Aspergillus nigrus, Fusarium oxysporum and Penicillium chrysogenum) and the concentration of the complex was kept at 0.5 mg ml^{-1} in DMSO and compared with known antibiotics viz



Fig. 8. ¹H NMR spectrum of Ni(dtc)₂ at different temperatures.

Tetracycline and Nystatin (Table 3) at the same concentration. The biological activity of Ni(II) dithiocarbamate complexes is well doc-

umented [36–41]. The agar well-diffusion method [42] was used for antibacterial and antifungal studies in this assay and each

Table 3

Mean zone of inhibition (mm ± stdev).

Antibacterial assay		Antifungal assay			
Bacteria	Ni(dtc) ₂	Tetracycline	Fungi	Ni(dtc) ₂	Nystatin
E. coli (mm ± stdev)	25.5 ± 0.5	17.0 ± 0.5	A. nigrus (mm ± stdev)	21.5 ± 0.5	18.0 ± 0.4
P. aeruginosa (mm ± stdev)	27.4 ± 0.6	15.0 ± 0.5	F. oxysporum (mm ± stdev)	27.4 ± 0.6	14.2 ± 0.4
B. thuringiensis (mm ± stdev)	31.0 ± 0.3	18.0 ± 0.4	P. chrysogenum (mm ± stdev)	24.0 ± 0.3	20.0 ± 0.5

experiment was performed in triplicate. The radial growth of the colony was recorded on completion of the incubation, and the mean diameter was recorded. The complex showed higher activity against the bacteria and fungi than the known antibiotics. Area of zone of inhibition was used as a criterion to ascertain the biocidal activity. The screening data are reported in Table 3. The 20 mm zone of inhibition represents significant activity, for 10-12 mm inhibition activity is good, 7-9 mm is low, and below 7 mm the activity is insignificant. The Ni(dtc)₂ shown remarkable antibacterial and antifungal activity against these pathogens.

5. Conclusion

The crystal structure of nickel(II) bis(N.N-diethyldithiocarbamate) has been revisited and refine up to R = 2.99%. This paper reports a rare Ni…H anagostic interaction evidenced by the crystal structure of Ni(dtc)₂. The complex showed higher antibacterial and antifungal activities than the slandered antibiotics. Ni(dtc)₂ showed highest activity for B. thuringiensis and F. oxysporum.

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Appendix A. Supplementary data

CCDC 682361 contains the supplementary crystallographic data for Ni(dtc)₂. This data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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