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Research paper

Novel ligands, benzophenone N(4)-methyl-N(4)-phenylthiosemicarbazone, 1-(amino-*N*-methylphenylmethanethio)(diphenylmethylene)thiocarbonohydrazide and the transition metal complexes of the latter

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ABSTRACT

Two Schiff base ligands, benzophenone N(4)-methyl-N(4)-phenylthiosemicarbazone (HL), 1-(amino-*N*-methyl-*N*-phenylmethanethio)(diphenylmethylene)thiocarbonohydrazide (H_2L') were synthesized. They were characterized by elemental analyses and spectral [Electronic, FT-IR, FT-Raman and ^{1}H NMR] studies. The structure of HL was determined by single-crystal X-ray diffraction studies. The complexes of Co(II), Ni(II), Cu(II) and Zn(II) of H_2L' were synthesized. They were characterized by the elemental analyses, magnetic susceptibility, IR, electronic, NMR and thermal (TGA) studies. The crystal structure of Ni$(HL')_2 \cdot 1.5H_2O$ was determined by single-crystal X-ray diffraction.

1. Introduction

Benzophenone derivatives are very important due to their versatile physicochemical properties such as electrochemical, spectroscopic, metal complexation, adsorptive and crystallographic properties [1,2]. They have the ability to absorb a broad range of UV radiation (200–350 nm). The benzophenone derivatives like 2-hydroxy-4-methoxybenzophenone are used as raw material in the manufacturing of sunscreen creams [3]. These creams are useful in various medical treatments to shun photosensitization, phototoxicity or allergic reactions of patients [4].

Topical studies have shown that benzophenone thiosemicarbazone exhibit inhibitory effects on parasites including *Trypanosoma brucei* and *Plasmodium falciparum* [5]. Schiff bases derived from benzophenone have been extensively studied for their cytotoxic activities against human oral squarnous carcinoma cells HSC-2 and normal human gingival fibroblasts (HGF). Antibiotic activities of these compounds against methicillin-resistant staphylococcus aureus and vancomycin-resistant Enterococcus faecium and protein kinase C inhibitor have been studied [6].

The main group- as well as transition metal complexes of thiosemicarbazones are of current importance by virtue of their interesting structural characteristics and diverse biological applications [7,8]. Benzophenone thiosemicarbazone containing π-electron conjugation system could act as one of the potential semi-organic optical materials. The flexible applications of benzophenone in different areas encouraged us to synthesize its N(4)-disubstituted thiosemicarbazone containing NS donor atoms. The metal ions used in this investigation are Co(II), Ni(II), Cu(II) and Zn(II), a few typical transition metal ions, the coordination compounds of which have immense structural, biological and industrial importance [9,10]. In this communication, we report the synthesis and characterisation of two compounds (HL) and (H_2L') derived from benzophenone and N(4)-methyl-N(4)-phenylthiosemicarbazide. In addition to this, crystal structure of (HL), synthesis and characterisation of transition metal complexes of (H_2L') and crystal structure of nickel complex are reported here.

2. Experimental details

All the chemicals used in the present study are of A.R grade. Metal salts were purchased from E. Merck and used as received.

2.1. Physical measurements

Elemental analyses (C, H, N and S) were performed on Vario EL III elemental analyzer. Infrared (IR) spectra were recorded on a

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Jasco-FT-IR-4100 model spectrometer using KBr pellets. The electronic spectra were recorded on JascoV-550 UV–Vis spectrometer. ^{1}H NMR spectra were recorded on 400 MHz Bruker NMR spectrometer. Magnetic susceptibility values of the complexes at room temperature were measured using Sherwood Scientific Magnetic Susceptibility Balance. TG/DTG was recorded on TGA Q50 V20.13 Build 39 model thermo gravimetric analyzer fitted with a thermal analysis controller in nitrogen atmosphere with a heating rate of 10 °C/min.

2.2. X-ray crystal determination

X-ray crystallographic data were collected at 296(2) K for HL and at 273(2) K for $Ni(HL')_2{\cdot}1.5H_2O$ on a Bruker Model Kappa Apex II diffractometer with graphite monochromatic Mo Kα (λ = 0.71073 Å) radiation. Direct methods were performed to solve the structure and refined by least-square on F^2 using SHELXL-97 for HL and SHELXL-2014/7 for nickel(II) complex. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms, except those attached to nitrogen were geometrically fixed at calculated positions. The crystallographic tools, PLATON for Windows [11], DIAMOND 3.2d, and MERCURY 3.5.1 [12] were used for structure analysis and presentation of the results. The structure was finally refined to the conventional *R*-value 0.0611 for HL and 0.0641 for Ni(II) complex.

2.3. Synthesis of ligands

(a) Synthesis of Benzophenone N(4)-methyl-N(4)-phenylthiosemicarbazone (HL)
N(4)-Methyl-N(4)-phenylthiosemicarbazide (MPTSC) was prepared by modifying the procedure reported by Scovill [13]. The compound was prepared by dropwise addition of a hot methanolic solution of benzophenone (.345 g, 1 mmol) into the boiling methanolic solution of N(4)-methyl-N(4)-phenylthiosemicarbazide (.182 g, 1 mmol) (MPTSC) taken in a round bottom flask. The reaction mixture was refluxed for 2 h. The volume of the solution was reduced and kept for overnight. The Schiff base compound obtained was filtered, washed with methanol, water and dried over anhydrous $CaCl_2$ (Fig. 1).

(b) Synthesis of 1-(aminophenylmethanethio)(diphenylmethylene)thiocarbonohydrazide (BP-MPTSC) (H_2L')
1-(AminoN-methyl-*N*-phenylmethanethio)(diphenylmethylene) thiocarbonohydrazide (H_2L') is prepared by dropwise addition of a hot methanolic solution of benzophenone (0.345 g, 1 mmol) to a boiling methanolic solution of MPTSC (0.364 g, 2 mmol) taken in a round bottom flask, 2 drops of glacial acetic acid was added to the reaction mixture and refluxed at 60–80 °C for 30 min. The solution was chilled and kept overnight. The cream coloured Schiff base ligand obtained was filtered and washed with methanol and dried (Fig. 2).

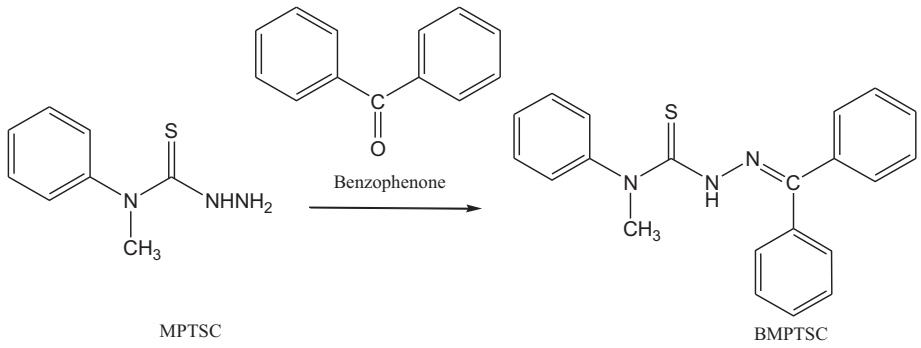

Fig. 1. The formation of Benzophenone N(4)-methyl-N(4)-phenyl thiosemicarbazone (BMPTSC) (HL).

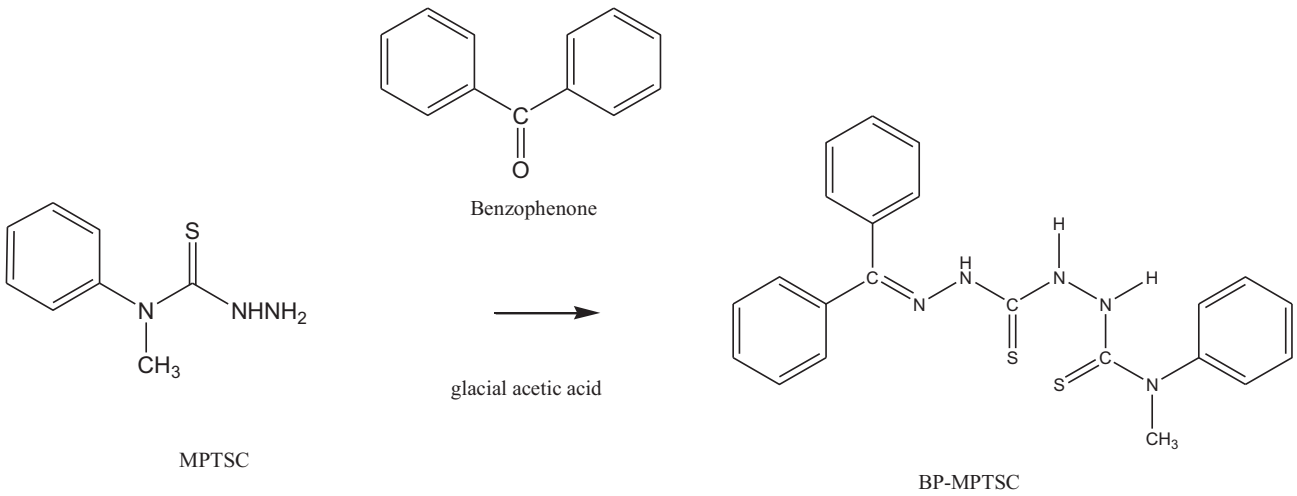

Fig. 2. The formation of 1-(AminoN-methyl-*N*-phenylmethanethio) (diphenylmethylene)thiocarbonohydrazide (BP-MPTSC) (H_2L').