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Preparation and characterization of pentagonal-bipyramidal zinc(II) and cadmium(II) complexes of a neutral N_3S_2 thiosemicarbazone derived from ^{2}N-methylthiosemicarbazide and the X-ray crystal and molecular structures of the free ligand and its cadmium(II) complex, Cd(dap-^{2}NMetsc)$(NO_3)_2$ ☆

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Abstract

A new pentadentate thiosemicarbazone has been synthesized and structurally characterized by spectroscopic and X-ray diffraction techniques. It reacts with zinc(II) and cadmium(II) nitrate producing crystalline complexes of general formula, [M(dap-^{2}NMetsc)$(NO_3)_2$] (M = Zn^{2}+, Cd^{2+}; dap-^{2}NMetsc = 2,6-diacetylpyridine bis(^{2}N-methylthiosemicarbazone)) which have been characterized by a variety of physico-chemical techniques. X-ray crystallographic structure determination of the free ligand shows that, in the solid state, it remains in the *E* form about the azomethine bonds with both the thione sulfur and pyridine nitrogen atoms *trans* to the azomethine nitrogen atoms. A single crystal X-ray structure determination of the [Cd(dap-^{2}NMetsc)$(NO_3)_2$] complex shows that the ligand is coordinated to the cadmium(II) ion *via* the two azomethine nitrogen atoms, the pyridine nitrogen atom and the two thione sulfur atoms. The thiosemicarbazone occupies the equatorial plane and the two nitrate ligands are coordinated to the cadmium atom as monodentate ligands occupying axial positions, the overall geometry of the complex being a distorted pentagonal-bipyramid.

Keywords: Pentadentate thiosemicarbazone; Pentagonal-bipyramidal zinc(II) and cadmium(II) complexes; Neutral N_3S_2 thiosemicarbazone

1. Introduction

There has been a large number of studies on metal complexes of tridentate thiosemicarbazones derived from α-N-heterocyclic carboxaldehydes and ketones [1–6]. Metal complexes of tetradentate thiosemicarbazones derived from α-ketoaldehydes and α-diketones have also received considerable attention [7–11] because of their significant biological activities. Metal complexes of pentadentate thiosemicarbazones are less common. However, in recent years there have been several reports on complexes of the 2,6-diacetylpyridine bis(thiosemicarbazone) (Fig. 1; dap-tsc; R,R$'$ = H) which has demonstrated its versatility as a chelating agent by forming different types of zinc(II) complexes depending on the reaction conditions and the types of zinc(II) salts used in the preparation of the complexes [12,13].

Three of the zinc(II) complexes of dap-tsc (Fig. 1; R,R$'$ = H) are dinuclear [12,13] but a fourth, [Zn(dap-tsc)$(H_2O)_2$] · H_2O is monomeric that contains seven-coordinated zinc atom in a pentagonal bipyramidal coordination environment [12]. Several seven-coordinate tin(IV) complexes of this ligand have also been structurally

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☆ dap-^{2}NMetsc = 2,6-diacetylpyridine bis(^{2}N-methylthiosemicarbazone).

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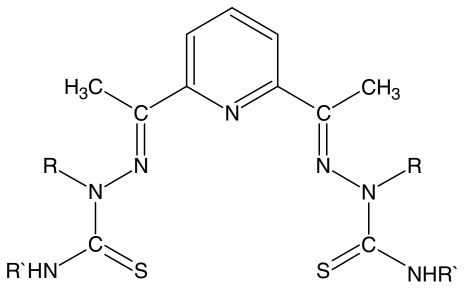

Fig. 1. 2,6-Diacetylpyridine bis(thiosemicarbazones).

characterized [14–18]. The related, 2,6-diacetylpyridine bis(^{4}N-methylthiosemicarbazone) (Fig. 1; R = H, R′ = CH_3) has also demonstrated its ability to act as a versatile chelating agent yielding a seven-coordinate manganese(II) complex [19], a five-coordinate lead(II) complex [20], a helical dimeric zinc(II) complex [20] and a seven-coordinate tin(II) complex [21].

Although pentagonal-bipyramidal complexes of zinc(II) [12], indium(III) [22], tin(IV) [14–18], tin(II) [21], iron(II) [22], bismuth(III) [23] of pentadentate N_3S_2 thiosemicarbazones have been well characterized, there does not seem to be a single report on seven-coordinate cadmium(II) complexes of a pentadentate thiosemicarbazone ligand. The only seven-coordinate cadmium(II) complex of a thiosemicarbazone that has been structurally characterized is $[Cd(HL^2)(Cl)_2(H_2O)_2]$ in which the HL^2 ligand is the 1:1 condensation product of 2,6-diacetylpyridine with thiosemicarbazide which behaves as an NNS tridentate chelating agent [24].

In view of limited structural and spectroscopic data available on seven-coordinate cadmium(II) complexes of pentadentate thiosemicarbazones and as part of our ongoing work on metal complexes of multidentate thiosemicarbazones, we report here the synthesis and characterization of new zinc(II) and cadmium(II) complexes of a neutral petadentate N_3S_2 thiosemicarbazone ligand, together with the X-ray crystal and molecular structures of the free ligand and its seven-coordinate cadmium(II) complex.

2. Experimental

2.1. Materials and instrumentation

All chemicals were of analytical reagent grades and used without any further purification. ^{2}N-Methylthiosemicarbazide was purchased from the Aldrich Chemical Company. The electronic spectra were recorded in solution on a Shimadzu UV-3100 spectrophotometer. The IR spectra were recorded as KBr discs on either a Perkin–Elmer 1600 FT IR spectrometer or a Perkin–Elmer 2000 spectrometer. Conductance measurements were made by means of a CMD 400 conductivity meter. The ^{1}H and ^{13}C NMR spectra were run in DMSO-d_6 on a Bruker Avance DPX 300 K FT NMR spectrometer using TMS as an internal standard.

2.2. Preparation of dap-^{2}NMetsc

2,6-Diacetylpyridine (1.63 g; 0.01 mol) was dissolved in boiling methanol (130 ml). Two drops of glacial acetic acid were added to the solution followed by the addition of a solution of ^{2}N-methylthiosemicarbazide (2.10 g; 0.02 mol) in methanol (100 ml). The reaction mixture was refluxed for three hours and then left to stand overnight. The yellow product that formed was filtered off, washed with cold methanol and dried in air. The crude compound was recrystallized from acetonitrile to afford crystals suitable for X-ray work. Yield: 2.30 g; 70%. *Anal.* Calc. for $C_{13}H_{19}N_7S_2$: C, 46.27; H, 5.67; N, 29.06. Found: C, 46.3; H, 5.66; N, 29.44%. NMR: δ_H(DMSO-d_6) 2.45 (6H, s, C–CH_3), 3.50 (6H, s, N–CH_3); 7.40 (s, br, NH_2); 8.34 (2H, d, pyH); 7.97 (1H, t, pyH), δ_C: (DMSO-d_6): 180.9 (C=S), 169.4 (pyC), 154.5 (pyC), 148.6 (C=N), 137.4 (pyC), 121.3 (pyC), 11.7 (CH_3), 41.9 (N–CH_3).

2.3. General method of preparation of $[M(dap\text{-}^2NMetsc)](NO_3)_2$ ($M = Zn^{2+}, Cd^{2+}$)

The hydrated metal(II) nitrate salt (1 mmol) dissolved in boiling methanol (30 ml) was mixed with a boiling solution of the ligand (1 mmol) in a mixture of methanol (150 ml) and dichloromethane (20 ml). The reaction mixture was heated under reflux for 1 h and then left to stand overnight. The complexes generally crystallized out of the reaction mixture as diffraction quality crystals. Yield: 70–80%. *Anal.* Calc. for [Zn(dap-^{2}NMetsc)$(NO_3)_2$] $C_{13}H_{19}N_9O_6S_2Zn$: C, 29.63; H, 3.63; N, 23.93. Found: C, 29.25; H, 3.73; N, 23.63%. δ_H(DMSO-d_6) 2.45 (6H, s, C–CH_3), 3.49 (6H, s, N–CH_3); 7.40 (s, br, NH_2); 8.30 (2H, d, pyH); 8.00 (1H, t, pyH), δ_C: (DMSO-d_6): 180.9 (C=S), 153.3 (C=N), 169.5, 168.3 (PyC), 126.4, 124.3, 123.5 (pyC); 138.9, 137.2 (pyC), 16.9, 16.8 (–CH_3), 41.9 (N–CH_3); Λ (ohm^{-1} cm^2 mol^{-1}) in DMF: 90.7.

Anal. Calc. for [Cd(dap-^{2}NMetsc)$(NO_3)_2$] ($C_{13}H_{19}N_9O_6Cd$): C, 27.20; H, 3.34; N, 21.96. Found: C, 27.11; H, 3.76; N, 21.39%. δ_H(DMSO-d_6): 2.63 (6H, s, C–CH_3), 8.60 (s, br, NH_2), 3.43 (6H, N–CH_3); 8.37 (2H, d, pyH);8.47 (1H, t, pyH); δ_C: (DMSO-d_6): 180.9 (C=S), 163.3 (pyC), 148.9 (C=N), 127.9 (pyC), 143.1 (pyC), 18.7 (CH_3); 43.77 (N–CH_3); Λ (ohm^{-1} cm^2 mol^{-1}) in DMF: 47.7.

2.4. Crystallography

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured on an Enraf-Nonius CAD 4 four-circle diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å) and operating in the ω–2θ mode within the range $2° < 2\theta < 50°$. An empirical absorption correction (ψ scans) [25] and data reduction [26] were performed within the WINGX [27] suite programmes. The structures were solved by direct methods with SHELX86 [28] and