

Metal Complexes of S-Acetyl(β -N-acetyl)dithiocarbazate

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The new ligand, S-acetyl(β -N-acetyl)dithiocarbazate ($\text{CH}_3\text{CONHNHCSSCOCH}_3$) reacts with metal ions only in alkaline medium as a bidentate uni-negative (N, S^-) donor ligand giving complexes of type $[\text{M}(\text{NS}^-)_2][\text{M} = \text{Ni(II) and Zn(II)}]$, $[\text{M}'(\text{NS}^-)_2\text{X}_2]$ [$\text{M}' = \text{Zr(IV) and Th(IV)}$; $\text{X} = \text{NO}_3^-$ and NCS^-], $[\text{Cr}(\text{NS}^-)_2\text{X} \cdot \text{H}_2\text{O}]$ and $[\text{UO}(\text{NS}^-)_2\text{X}_2]$. Analytical, conductivity and magnetic measurements, and spectral data of the complexes are consistent with four-coordination of Ni(II) and Zn(II) ions while zirconium, thorium and chromium analogues are six-coordinate. The uranium complexes are seven-coordinate.

Coordination properties of a number of novel N_2O or $\text{N}_2\text{O}_2\text{S}$ donor ligands have been reported from our laboratory¹⁻⁷. As a part of our general study of N_2S ligands, we report herein the synthesis and characterization of new complexes of Ni(II), Zn(II), Zr(IV), Th(IV), Cr(III) and U(VI) with a bidentate, S-acetyl(β -N-acetyl)dithiocarbazate.

Materials and Methods

Infrared spectra were recorded in KBr on a Pye-Unicam SP3-300 infrared spectrophotometer, electronic spectra on a LKB-Ultrospec K4053 spectrophotometer, PMR spectra in CDCl_3 on a Varian XL-300 spectrophotometer using TMS as an internal standard and mass spectra on a Hitachi RMU-6D instrument operating at 70 eV. Conductivities of 10^{-3} M solutions of the complexes were measured at $\sim 25^\circ\text{C}$ in dimethyl sulfoxide (DMSO) using a WPA CM35 conductivity meter fitted with a dip-cell and platinized electrodes. Magnetic susceptibilities were measured at room temperature by the Faraday method. Diamagnetic corrections for the constituent elements were obtained using Pascal's constants⁸.

Preparation of S-acetyl(β -N-acetyl)dithiocarbazate (SADTC)

To a solution of potassium hydroxide (11.4 g) in 90% ethanol (70 ml) was added hydrazine hydrate (10 g) and the mixture was cooled to 0°C . Carbon disulfide (15.2 g) was added dropwise to the above mixture with constant stirring during 1 hr, the light brown layer was separated, dissolved in cold 40% ethanol (60 ml), kept in an ice-bath and acetyl chloride (25 g) was added to it dropwise with vigorous stirring. A white product which separated out was filtered, washed with water, dried, recrystallized from ethanol and dried over P_4O_{10} ; yield

10.5 g (Found: C, 31.1; H, 4.2; S, 33.0. $\text{C}_5\text{H}_8\text{N}_2\text{S}_2\text{O}_2$ requires C, 31.2; H, 4.2; S, 33.3%; IR: 3310 (νNH), 1620 ($\nu\text{C}=\text{O}$), 1090 ($\nu\text{C}=\text{S}$) cm^{-1} ; PMR: δ 3.35 (3H, CH_3), 7.3 (ArH), 10.2 (NH); MS: m/z 192, 160, 149, 128, 77, 64, 57, 43, 32.

(a) Preparation of $[\text{M}(\text{NS})_2][\text{M} = \text{Ni(II)}]$ (complexes 1 and 2), $[\text{M}(\text{NS})_2(\text{NO}_3)_2]$ [$\text{M}' = \text{Zr(IV) and Th(IV)}$] (complexes 3 and 5), $[\text{Cr}(\text{NS})_2\text{NO}_3 \cdot \text{H}_2\text{O}]$ (complex 7) and $[\text{UO}(\text{NS})_2(\text{NO}_3)_2]$ (complex 9); [NS = deprotonated form of SADTC]

SADTC (0.008 mol) was added to aq. potassium hydroxide (0.008 mol in 30 ml water), stirred for 5 min, filtered, and to the filtrate was added, with stirring, a solution of a metal nitrate (0.004 mol) in water (20 ml) and heated on a water-bath for 20 min. The resulting precipitate was filtered, washed with water and ethanol and dried *in vacuo* over P_4O_{10} .

(b) Preparation of $[\text{M}'(\text{NS})_2(\text{NCS})_2]$ [$\text{M}' = \text{Zr(IV) and Th(IV)}$] (complexes 4 and 6), $[\text{Cr}(\text{NS})_2(\text{SCN})\text{H}_2\text{O}]$ (complex 8) and $[\text{UO}(\text{NS})_2(\text{NCS})_2]$ (complex 10)

To a solution of hydrated metal nitrate (0.004 mol) in anhydrous methanol (30 ml) was added a solution of potassium thiocyanate (0.016 mol) in the same solvent (25 ml). The precipitated potassium nitrate was filtered, the filtrate added to an aqueous solution (30 ml) of SADTC (0.004 mol) containing potassium hydroxide (0.008 mol). The precipitate obtained was filtered, washed with water and ethanol and dried *in vacuo* over P_4O_{10} .

Results and Discussion

The analytical data of the complexes are given in Table 1. The electrical conductivities of 10^{-3} M

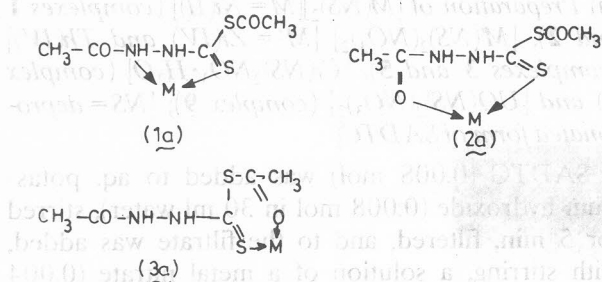
Table 1—Characterization Data of Complexes^a

Compd	Colour	Found (Calc) %		
		M ^a	C	H
[Ni(CH ₃ CONHNCSSCOCH ₃) ₂](1)	Buff	13.2(13.3)	27.2(27.2)	3.1(3.2)
[Zn(CH ₃ CONHNCSSCOCH ₃) ₂](2)	Colourless	14.6(14.6)	26.6(26.8)	3.1(3.1)
[Zr(CH ₃ CONHNCSSCOCH ₃) ₂ (NO ₃) ₂](3)	-Do-	15.2(15.3)	19.8(20.1)	2.3(2.3)
[Zr(CH ₃ CONHNCSSCOCH ₃) ₂ (NCS) ₂](4)	-Do-	15.2(15.5)	24.2(24.4)	2.3(2.4)
[Th(CH ₃ CONHNCSSCOCH ₃) ₂ (NO ₃) ₂](5)	-Do-	31.2(31.4)	16.0(16.3)	1.9(1.9)
[Th(CH ₃ CONHNCSSCOCH ₃) ₂ (NCS) ₂](6)	-Do-	31.4(31.8)	19.6(19.7)	1.9(1.9)
[Cr(CH ₃ CONHNCSSCOCH ₃) ₂ (NO ₃) ₂ ·H ₂ O](7)	Blue	10.0(10.1)	23.1(23.3)	3.1(3.1)
[Cr(CH ₃ CONHNCSSCOCH ₃) ₂ (SCN)·H ₂ O](8)	-Do-	10.0(10.2)	25.8(25.9)	3.0(3.1)
[UO(CH ₃ CONHNCSSCOCH ₃) ₂ (NO ₃) ₂](9)	Yellow	31.0(31.3)	15.5(15.8)	1.8(1.8)
[UO(CH ₃ CONHNCSSCOCH ₃) ₂ (NCS) ₂](10)	-Do-	31.5(31.7)	19.0(19.1)	1.8(1.9)

(^a)Ni(II) and Zn(II) were determined gravimetrically (as dimethylglyoximate complex) and complexometrically (with EDTA) respectively²³. Zr(IV)¹³, Th(IV)¹² and U(VI)¹¹ were determined gravimetrically as oxides after complete ignition of the complexes.

solutions in DMSO indicated that the complexes were non-electrolytes suggesting that the anions were coordinated in all the complexes.

The ligand SADTC is a potential bidentate ligand and sterically favourable three types of coordinations (**1a**, **2a** and **3a**) are possible.



In the IR spectra of the complexes the $\nu(\text{CO})$ mode of the free ligand remains unchanged excluding structures (**2a**) and (**3a**). SADTC reacts with metal ions only in alkaline medium. Attempts to prepare complexes from a neutral medium were unsuccessful. This suggests that nucleophilicity of the ligand is greatly enhanced in alkaline medium probably due to creation of an anionic site *in situ*^{1,3,4,6}. Presumably, the ligand exists in thione and thiol tautomeric forms (**1b**) and (**1c**) although the PMR spectrum does not show any SH proton indicating that **1b** is the predominant form. However, the non-electrolytic and diamagnetic nature of [Ni(NS⁻)₂](**1**) provide strong evidence that in alkaline medium the ligand is deprotonated and bonding occurs through the thiolate anion, generated from thiol (**1c**), causing spin-pairing in the complex⁹. Similar observations were made for complexes of S-benzoyl (β -N-benzoyl)dithiocarbamate, (C₆H₅CONHNCSSCOC₆H₅)¹⁰. Besides, the IR spectra of **1-10** indicate shift of $\nu(\text{C}=\text{S})$ mode

of the free ligand and a sharp band at 1570-1550 cm⁻¹, attributable to $\nu(\text{C}=\text{N})$ mode. The β -nitrogen coordination is evident from the shift of $\nu(\text{NH})$ of the free ligand appearing at 3310 cm⁻¹ to lower wavenumbers (3080-3250 cm⁻¹) in **1-10**. The far IR spectra of the complexes exhibit bands in the region 460-275 and 350-230 cm⁻¹ which are tentatively attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ modes [M=Ni(II), Zn(II), Zr(IV), Th(IV), Cr(III) and U(VI)], respectively^{1,4,5,11-16}. The IR spectra of **3**, **5**, **7** and **9** exhibit bands at about 1490, 1285, 1010 and 810 cm⁻¹ characteristic of unidentate nitrate group^{5,15}. The complexes **4**, **6**, **9** and **10** exhibit intense band in the region 2000-2050 cm⁻¹ assignable to $\nu(\text{C}\equiv\text{N})$ mode. This suggests that thiocyanate is coordinated through the nitrogen indicating that Zr(IV), Th(IV) and U(VI) behave as class A acceptors^{17,18}. The complex **8**, however, shows $\nu(\text{C}\equiv\text{N})$ at 2115 cm⁻¹ arising from S-coordinated thiocyanato moiety^{17,18}. Unexpectedly it indicates that Cr(III) is a softer acid than Zr(IV) and Th(IV). This is attributed to the higher ionization potentials¹⁹ of Zr(IV) and Th(IV) compared to that of Cr(III) making the former ions more acidic than the latter. The uranium complexes **9** and **10** display band at 915 cm⁻¹ due to $\nu(\text{U}=\text{O})$ mode¹⁰. Complexes **7** and **8** show broad band around 3380 cm⁻¹ arising from coordinated water molecule¹¹⁻¹³.

All of the complexes, except those of chromium, are diamagnetic. The chromium complexes **7** and **8** have magnetic moments of 3.99 and 4.02 B.M., respectively corresponding to three unpaired electrons. The electronic spectra of zinc, zirconium, thorium and uranium complexes exhibit a single band in the region 280-350 nm due to charge transfer transition. The electronic spectrum of the nickel complex **1** is consistent with a square-planar geometry^{20,21}. The ob-

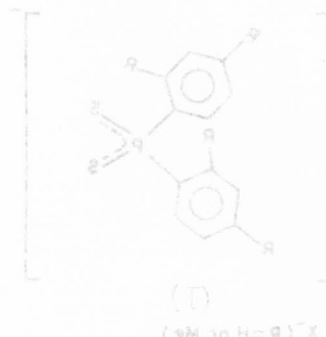
served absorptions at 520, 395 and 320 nm correspond to $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_g$ transitions in D_{4h} symmetry, respectively. The chromium complexes **7** and **8** exhibit three bands at around 550, 430 and 380 nm corresponding to $^4A_{2g} \rightarrow ^4T_{2g}$, $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{1g}(P)$ transitions in O_h symmetry, respectively^{20,22}.

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(I)

X = H or Me

Materials and Methods

All the chemicals used were of AR grade. Dithiocarbazic acids were synthesized by the method described before.¹