

SYNTHESIS AND CHARACTERIZATION OF COBALT(III) DITHIOCARBAMATE COMPLEXES

G. Gurumoorthy

Department of Chemistry, Bharath Institute of Higher Education and Research, Chennai

gurugovindchem@gmail.com

Abstract

Tris(N-(pyrrol-2-ylmethyl)-N-butylthiocarbamate-S,S')cobalt(III) (1), tris(N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl)dithiocarbamate-S,S')cobalt(III) (2) and tris(N-methylferrocenyl-N-(2-phenylethyl)dithiocarbamate-S,S')cobalt(III) (3) have been synthesized and characterized by elemental analysis and spectroscopy (IR, UV-vis and NMR). The elemental analysis and IR, ¹H and ¹³C NMR spectra are consistent with the formation of the cobalt(III) complexes with dithiocarbamate ligands.

Key words: Cobalt(III) dithiocarbamate

Introduction

A wide range of metal-dithiocarbamate complexes is known with examples finding use in applications as diverse as industry, agriculture, medicine and material science [1-7]. Metal sulfide nanoparticles have shown vital applications in many fields as advanced materials such as IR detectors [6], photocapacitors for energy conversion and storage [7], sensors [8], photonic materials [9] and advanced optoelectronic devices [10]. In recent years, transition metal dithiocarbamate complexes have received a great deal of attention because of their importance as single source precursors for the preparation of metal sulfide nanoparticles [11,12]. The N-bound organic moieties in dithiocarbamate ligands in metal complexes affect the morphology and size of the metal sulfide nanoparticles [13,14]. These nanoparticles have been used for the photocatalytic degradation of various organic pollutants such as dyes, p-nitrophenol *etc.*[15,16]. The photocatalytic activity of the metal sulfide nanoparticles depends on the morphology and size of the nanoparticles [17]. Furthermore, transition metal dithiocarbamates containing redox active ferrocene moiety are used as sensors for anions [18,19]. Particularly, cobalt(III) dithiocarbamate complexes have been used as catalyst for the synthesis of β -enaminoesters and β -enaminones from 1,3-diketones and β - ketoesters [20], sensor for ions [21] and single source precursor for the preparation of metal sulfide nanoparticles [22]. Our aim is to prepare cobalt(III) dithiocarbamate complexes for the sensing of anions and preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles. In this paper we report, synthesis and characterization of complexes **1-3** and their utilization of **3** for anion sensing and in addition, preparation of cobalt sulfide and cobalt-iron sulfide nanoparticles from complexes **2** and **3** and their photocatalytic behavior for dye degradation are presented.

2. Experimental

2.1. Materials and techniques

All reagents and solvents were commercially available high-grade materials (Merck/ Sd fine/Sigma aldrich) and used as received. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range: 4000–400 cm⁻¹) as KBr pellets. A Shimadzu UV-1650 PC double-beam UV-vis spectrophotometer was used for recording the electronic spectra. The spectra of complexes were recorded in CHCl₃ and the pure solvent was used as the reference. The NMR spectra were recorded on Bruker 500 MHz NMR spectrometers at room temperature in DMSO-d₆, using TMS as internal reference.

3. Preparation of complexes

Preparation of amines

N-(pyrrol-2-ylmethyl)-N-butylamine, N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl)amine and N-methylferrocenyl-N-(2-phenylethyl)amine were prepared by general methods reported earlier [12].

3.1. Preparation of 1

N-(pyrrol-2-ylmethyl)-N-butylamine (3.0 mmol) in ethanol was mixed with carbon disulfide (3.0 mmol) under ice cold condition (5 °C). The solution was stirred for 30 min. This produced the (N-(pyrrol-2-ylmethyl)-N-butyl)dithiocarbamic acid solution. An aqueous solution of CoCl₂·6H₂O (1.0 mmol) was added to the dithiocarbamic acid solution resulting in the formation of a green precipitate. The precipitate obtained was filtered, washed several times with cold water and then air dried (Scheme-1). Yield: 78 %, mp: 155-156°C. IR (KBr, cm⁻¹): $\nu = 3380$ ($\nu_{\text{N-H}}$), 1488 ($\nu_{\text{C-N}}$), 1027 ($\nu_{\text{C-S}}$). UV-Vis (CHCl₃, nm): $\lambda = 250, 277, 327, 400, 488, 642$; ¹H NMR (500 MHz, DMSO-d₆): δ 0.98 (b, 9H, N-CH₂-CH₂-CH₂-CH₃), 1.38 (b, 6H, N-CH₂-CH₂-CH₂-CH₃), 1.68 (b, 6H, N-CH₂-CH₂-CH₂-CH₃), 3.65 (6H, N-CH₂-CH₂-CH₂-CH₃), 4.67- 5.02 (m, 6H, N-CH₂ (pyrrole)), 6.15 (s, 3H, H-3(pyrrole)), 6.20 (s, 3H, H-4, (pyrrole)), 6.81 (s, 3H, H-5(pyrrole)), 9.04 (3H, NH-pyrrole). ¹³C NMR (125 MHz, DMSO-d₆): δ 13.7 (N-CH₂CH₂CH₂CH₃), 20.1 (N-CH₂-CH₂-CH₂-CH₃), 28.9 (N-CH₂-CH₂-CH₂-CH₃), 44.7 (N-CH₂-CH₂-CH₂-CH₃), 48.1 (N-CH₂ (pyrrole)), 107.8, 109.4, 119.1, 125.6 (pyrrole ring carbons), 205.6 (NCS₂). Anal. Calcd. for C₃₀H₄₅CoN₆S₆, (%): C, 48.62; H, 6.12; N, 11.34; found (%): C, 48.49; H, 6.08 ; N, 11.24 .

3.2. Preparation of 2

A method similar to that described for the synthesis of 1 was adopted; however, N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl)amine was used instead of N-(pyrrol-2-ylmethyl)-N-butylamine (Scheme 1). Yield: 82%, mp: 150-152°C, IR (KBr, cm⁻¹): $\nu = 3382$ ($\nu_{\text{N-H}}$), 1485 ($\nu_{\text{C-N}}$), 1028 ($\nu_{\text{C-S}}$). UV-Vis (CHCl₃, nm): $\lambda = 251, 278, 326, 398, 482, 642$, ¹H NMR (500 MHz, DMSO-d₆): δ 2.99 (6H, NCH₂-CH₂-C₆H₅), 4.69 (6H, NCH₂-CH₂-C₆H₅), 4.81 (6H, NCH₂-(Pyrrole)), 6.20 (6H, H-3 and H-4 (pyrrole)), 6.80 (3H, H-5, (pyrrole)), 7.23-7.36 (15H, phenyl ring protons), 8.91 (3H, NH-pyrrole), ¹³C NMR (125 MHz, DMSO-d₆): δ 33.3 (N-CH₂-CH₂-C₆H₅), 45.6 (N-CH₂CH₂-C₆H₅), 50.2 (N-CH₂-(Pyrrole)), 108.0, 109.6, 119.4, 125.3, (pyrrole ring carbons), 126.7, 128.6, 129.0, 137.6 (phenylring carbons), 205.2 (NCS₂). Anal. Calcd. for C₄₂H₄₅CoN₆S₆ (%): C, 56.99; H, 5.12; N, 9.49; found (%): C, 56.72 ; H, 5.13 ; N, 9.43.

3.3. Preparation of 3

A method similar to that described for the synthesis of 1 was adopted; however, N-methylferrocenyl-N-(2-phenylethyl)amine used instead of N-(pyrrol-2-ylmethyl)-N-butylamine (Scheme 1) Yield: 84%, mp: 165-166°C. IR (KBr, cm⁻¹): $\nu = 1485$ ($\nu_{\text{C-N}}$), 1025 ($\nu_{\text{C-S}}$). UV-Vis (CHCl₃, nm): $\lambda = 249, 274, 323, 401, 472, 632$; ¹H NMR (500 MHz, DMSO-d₆): δ 2.91 (N-CH₂-CH₂-C₆H₅), 3.65-4.80 (NCH₂-CH₂-C₆H₅, N-CH₂ ferrocenyl and cyclopentene), 7.24 (b, 15H, phenyl ring protons) ¹³C NMR (125 MHz, DMSO-d₆): δ 33.4 (N-CH₂-CH₂-C₆H₅), 47.9 (N-CH₂-CH₂-C₆H₅), 49.2 (N-CH₂-ferrocenyl), 68.6, 68.8, 70.1, 80.1 (C-C (ferrocenyl ring carbons) 126.5, 128.6, 128.8, 138.3 (phenyl ring carbons), 205.0 (NCS₂). Anal. Calcd. for C₆₀H₆₀CoFe₃N₃S₆ (%): C, 58.02; H, 4.87; N, 3.38; found (%): C, 58.00; H, 4.84 ; N, 3.37.

4. Results and discussion

4.1 Spectral studies of 1-3

4.1.1 IR spectral studies

IR spectra of the metal dithiocarbamate complexes are useful analytical tool to find the coordination mode (monodentate or bidentate) of dithiocarbamate ligands [24]. In the case of bidentate ligand a solitary band is observed in the region of 950-1050 cm^{-1} while the splitting of this band within narrow range of 20 cm^{-1} is due to the monodentate coordination of dithiocarbamate ligand. Only one band associated with the C-S stretching is observed around 1027 cm^{-1} for **1-3** in the IR spectra confirming the bidentate coordination mode of the ligands. The spectral region from 1450-1500 cm^{-1} is associated with the $\nu_{\text{C-N}}$ (thioureide) vibrational mode. For complexes **1-3**, the ($\nu_{\text{C-N}}$) (thioureide) were found around 1485 cm^{-1} , indicating the partial double bond character.

4.1.2 NMR spectral studies

^1H NMR spectral studies

The protons of methylene group attached to pyrrole group in complexes **1** and **2** appear around 4.75 ppm. The remaining three and two signals in the aliphatic region of **1** and **2**, respectively are due to the butyl and ethyl groups; that shifted to lower field being nitrogen bound. NH protons of pyrrole rings are observed around 9.00 ppm. The methylene protons of ferrocenyl methyl, NCH_2 protons of $\text{NCH}_2\text{CH}_2\text{C}_6\text{H}_5$ and ferrocene ring protons are appeared in the region 3.65-4.80 ppm for complex **3**. Aromatic proton signals for all the complexes **1-3** are appeared in the region 6.15-7.30 ppm. The expected splitting patterns were not observed in these complexes. This is due to the paramagnetic nature of the complexes [25].

^{13}C NMR spectral studies

For complexes **1** and **2**, the signals for methylene carbon attached pyrrole $\text{NCH}_2\text{CH}_2\text{C}_6\text{H}_5$ and NCH_2 (butyl) carbons are observed in the region 45-50 ppm. The other signals appeared in the aliphatic region of **1** and **2** are assigned to the remaining carbons of methylene of butyl and phenyl ethyl groups. In the case of complex **3**, the signals observed at 33.4, 47.9 and 49.2 ppm are due to methylene carbon of $\text{N-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$, ferrocenyl methyl group, $\text{N-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$ and, respectively. Ferrocene ring carbons resonate in the region 68.5-77.2. The important ^{13}C NMR chemical shift value of the thioureide carbon (N^{13}CS_2) observed in the region 204.9-205.6 ppm, indicating contribution of double bond character to a formally single N-C bond in the dithiocarbamates.

4.1.3. Electronic spectral studies

UV-vis spectra of metal-dithiocarbamate complexes usually show three absorption bands in the ultraviolet region due to $\pi\text{-}\pi^*$ transition of NCS and SCS moiety and $n\text{-}\pi^*$ transition (i.e. transfer of a electron of the lone pair on the S to an antibonding π -orbital) [26]. In the present study, these three bands are observed around 250, 275 and 325 nm. A band appeared around 400 nm is due to either metal \rightarrow ligand or ligand \rightarrow metal charge transfer. Complexes **1-3** show two bands in the visible region 630-645 and 470-485 nm due to d-d transitions. The absorption pattern suggests octahedral coordination around Co(III) [27].

5. Conclusions

In this contribution three new cobalt(III) dithiocarbamate complexes have been synthesized and characterized by spectroscopic techniques. UV-vis spectra data are consistent with the formation of octahedral cobalt(III) complexes.

References

1. Z. Leka, D. Voja, M. Kosovic, N. Latinovic, M. Dakovic, A. Visnjevac, Synthesis, structure and antifungal activities of noval Co, Mo and Pt complexes with triammonium N,N-diacetatedithiocarbamate, *Polyhedron*. 80 (2014) 233- 242:
2. G.N. Kaludjerovic, V.M. Ojinovic, S.R. Trifunovic, I.M. Hodzic and T.J. Sabo, Synthesis and characterization of tris[butyl-(1-methyl-3-phenyl-propyl)-dithiocarbamate]-cobalt(III)seskvitoluene, *J. Serb. Chem. Soc.* 67 (2002) 123-126:
3. R. Abu-El-Halawa, S.A. Zabin, Removal efficiency of Pb, Cd, Cu and Zn from polluted water using dithiocarbamate ligands, *J. Taiba Univ. Sci.* (2015) 1- 9:
4. H. Nabipour, S. Ghammamy, S.Ashuri, Z.S. Aghbologh, Synthesis of a New Dithiocarbamate Compound and Study of Its Biological Properties, *Org. Chem. J* 2 (2010) 75-80:
5. A.C. Costa Junior, O.Versiane, G.Faget Ondar, J.M. Ramos, G.B. Ferreria, A.A. Martin, C.A. Tellez soto, An experimental and theoretical approach of spectroscopic and structural properties of the bis(diethylthiocarbamate)-cobalt(II), *J. Mol. Struct.* 1029 (2012) m119-134:
6. J. Masek, I. Ishida and H. Zogg, C. Maissen, S. Blunier, Monolithic photovoltaic PbS-on-Si infrared-sensor array, *IEE Electr. Dev. Lett.* 11 (1990) 12-14:
7. M. Gong, A. Kiokeminde, N.Kumar, H.Zhao and S.Ren, Ionic-passivated FeS₂ photocapactors for energy conversion and storage, *Chem. Commun.* 49 (2013) 9260-9262:
8. N. Tokyo, K. Azkio, *J. Ph. Kokai Pat.* 7855478 C1.C23 C15/00, (1978).
9. N. Tokya, *J. Ph. Kokai pat.* 75130378 C1 H0 1L CO 1B, (1975).
10. D. J. Asunskis, I.L. Boltin, A. T. W Rolde, A.M. Zachary and L.Hanley, Lead sulfide nanocrystals-polymer composition for optoelectronic applications, *Macromol. Symp.* 268 (2008) 33-37:
11. S. Khalid, E. Ahmed, M.A. Malik, S. Abu bakar, Y. Khan and P.O. Brien, Synthesis of pyrite thin films and transition metal doped pyrite thin films by aerosol-assisted chemical vapour deposition, *New. J. Chem.* 39 (2015) 1013-1021:
12. E. Sathiyaraj, G. Gurumoorthy and S. Thirumaran, Nickel(II) dithiocarbamate complexes containing the pyrrole moiety for sensing anions and synthesis of nickel sulfide and nickel oxide nanoparticles, *New.J.Chem.* 39 (2015) 5336-5349:
13. N.L. Pickett and P.O.Brien, Synthesis of semiconductor nanoparticles using single-molecular precursors, *Chem. Rec.* 1 (2001) 467-479:
14. N. Srinivasan, S. Thirumaran, Effect of pyridine as a ligand in precursor on morphology of CdS nanoparticles, *Superlattices Microstruct.* 51 (2012) 912-920:
15. N. Soltani, E. Saion, M.Z. Hussein, M. Erfani, A. Abedini, G. Bahmanrokh, M. Navasery and P.Vaziri, Visible light- induced degradation of methylene blue in the presence of photocatalytic ZnS and CdS nanoparticles, *Int. J. Mol. Sci.* 13 (2012) 12242-12258:
16. Y. Wada, T.Kitamura, S. Yanaqida and H. Yin, Photoreduction dechlorination of chlorinated benzene derivatives catalyzed by ZnS nano crystallites, *Chem. Commun.* (1998) 2683-2684:

17. S. Rengaraj, S. Venkatraj, S.H. Jec, Y.H. Kim, C. Tai, E. Repo, A. Koistinen, A. Ferancova, M. Sillpaa, Self-Assembled Mesoporous Hierarchical-like In₂S₃ Hollow Microspheres Composed of Nanofibers and Nanosheets and their Photocatalytic Activity, *Langmuir* 27 (2011) 352- 358:
18. W.W.H. Wong, D. Curiel, S.W. Lai, M. G. B. Drew and P. D. Beer, Ditopic redox-active poly ferrocenyl zinc (II) dithiocarbamate macrocyclic receptors: synthesis, coordination and electrochemical recognition properties, *Dalton Trans.* 4 (2005) 774-781:
19. P. D. Beer and D. K. Smith, Tunable bis(ferrocenyl) receptors for the solution- phase electrochemical sensing of transition-metal cations, *J. Chem. Soc, Dalton Trans.* (1998) 417-423:
20. P. Bharati, A. Bharti, P.Nath, M.K. Bharty, R.J. Butcher, N.K. Singh, Synthesis, spectral and structural characterization of cobalt (III) dithiocarbamate complexes: catalytic application for the solvent free enamination reaction, *Polyhedron* 102 (2015) 375-385:
21. P.D. Beer, N.G. Berry, A.R.Cowley, E.J. Hayer, E.C. Oates and W.W.H. Wong, Metal-directed self-assembly of bimetallic dithiocarbamate transition metal cryptands and their binding capabilities, *Chem. Commun.* (2003) 2408-2409:
22. H. Cui, R.D. Pike, R. Kershaw, K. Dwight, A. Wold, Synthesis of Ni₃S₂, Co₉S₈ and ZnS by the decomposition of diethyldithiocarbamate complexes, *J. Solid State Chem.* 101 (1992) 115-118:
23. S.K. Verma, V.K. Singh, Synthesis and characterization of ferrocene functionalized transition metal dithiocarbamate complexes: investigations of antimicrobial, electrochemical properties and a new polymorphic form of [Cu{K₂S₂S-S₂CN(CH₂C₄H₃O)CH₂Fc}₂], *J. Organomet.Chem.* 791 (2015) 214-224:
24. S.A.A. Nami, I. Ullah, M. Alam, Dond-Ung Lee, N. Sarikavakli, Synthesis characterization, molecular docking and biological studies of self assembled transition metal dithiocarbamates of substituted pyrrole-2-carboxaldehyde, *J Photochem Photobiol B.* 160 (2016) 392-399:
25. M.D. Fryzuk, D.B. Leznoff, R.C. Thompson and S.J. Rettig, One- electron transformations of paramagnetic cobalt complexes: synthesis and structure of cobalt(II) Amidophosphine halide and alkyl complexes and their reaction with alkyl halides, *J. Am. Chem. Soc.* 120 (1998) 10126-10135:
26. I. P. Ferreira, G. M. de Lima, E. B. Paniago, J. A. Jakahashi, K. Krambrock, C. B. Pinheiro, J. I. Wardell, L. C. Visentin, Synthesis, characterisation, structural and biological aspects of copper(II) dithiocarbamate complexes-part II, [Cu{S₂CN(Me)(R₁)₂}], [Cu{S₂CN(Me)(R₂)₂}] and [Cu{S₂CN(R₃)(R₄)₂}] {R₁ = CH₂CH(OMe)₂, R₂ = 2-methyl-1,3-dioxolane, R₃ = CH₂(CH₂)₂N = CHPhOCH₂Ph and R₄ = -CH₂CH₂OH}, *J. Mol. Struct.* 1048 (2013) 357-366:
27. R. Dulare, M. K. Bharty, A. Singh, A. K. Singh, Synthesis, spectral and structural studies of 1-ethoxycarbonyl-piperazine- 4-carbodithioate and its Co(III), Zn(II) and Cd(II) complexes, *Polyhedron.* 31 (2012) 373-378: