Research Article

Synthesis and Characterization of the Adducts of Bis(O-ethylthiocarbonato)copper(II) with Substituted Pyridines

Gurpreet Kour, Inderjeet Kour, and Renu Sachar

Department of Chemistry, University of Jammu, Babasaheb Ambedkar Road, Jammu Tawi, Jammu 180006, India

Correspondence should be addressed to Gurpreet Kour; gurpreetkour94@yahoo.com

Received 22 August 2013; Revised 29 October 2013; Accepted 12 November 2013

Academic Editor: Alfonso Castiñeiras

Copyright © 2013 Gurpreet Kour et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Monomeric five coordinated adducts of bis(O-ethylthiocarbonato)copper(II) of general formula $[\text{Cu}(\text{C}_2\text{H}_5\text{OCS}_2)_2(\text{L})]$, $[\text{L} = 2\text{-}, 3\text{-}, 4\text{-methylpyridines and } 2\text{-}, 3\text{-}, 4\text{-ethylpyridines}]$ have been synthesized and characterized by elemental analysis, i.r. and electronic spectroscopy, magnetic and conductivity measurements. Analytical results show that the adducts have 1:1 stoichiometry. The adducts were found to be paramagnetic and their magnetic moments at room temperature lie within the 1.81–1.94 B.M. range and this indicates the presence of one unpaired electron. All the adducts have distorted square pyramidal geometry.

1. Introduction

O-Alkylthiocarbonates, popularly known as xanthates derivatives, have found a wide practical application as addition to lubricating oils, antioxidants for polyolefins, and so forth. However, alkylxanthates are mainly used in flotation concentration of nonferrous metal sulfide ores. These are extensively used as pharmaceuticals, fungicides, pesticides, and quite recently in therapy for HIV infections [1–3]. Divalent transition metals xanthates are partly unsaturated and can therefore form 1:1 adducts with electron donors such as neutral nitrogen, oxygen, phosphorus, or sulfur donors in which the coordination geometry ranges from square pyramidal to trigonal bipyramidal [4]. Such adducts of many transition metals such as Ni, Zn, Mn, V, Pt, and Pd are well studied, but little attention has been paid to the xanthates of copper owing to their instability. Here we report synthesis and investigation of the 1:1 adducts of some adducts of copper(II)xanthates with substituted pyridines such as 2-, 3-, 4-methylpyridines and 2-, 3-, 4-ethylpyridines.

2. Experimental

2.1. Preparation of Potassium Salt of O-ethylthiocarbonate. Potassium salt of ethyl xanthate was prepared by the method

reported in literature [5]. Into a 500 mL round bottomed flask, fitted with a reflux condenser, was placed 0.75 mole of potassium hydroxide pellets and 120 g of ethanol. The reaction mixture was heated under reflux for 1 hour. The mixture was then cooled and liquid from the residual solid was decanted off into another dry 500 mL flask. To this flask was added 45 mL (0.75 mole) of carbon disulfide slowly with constant shaking. The residual solid yellow mass was filtered (after cooling in ice) on a sintered glass funnel at the pump. It was washed with three 25 mL portions of ether. The resulting potassium salt of ethyl xanthate was dried in a vacuum desiccator over anhydrous calcium chloride. The yield was about 75 g. It was then recrystallized from ether.

2.2. Preparation of Adducts of Bis(O-ethylthiocarbonato)copper(II) with Substituted Pyridines. The yellow coloured parent compound copper(II)xanthate could not be isolated because it changed rapidly into brown coloured copper(I)xanthate. The addition complexes were prepared by the direct reaction of solution of metal salt, solution of potassium salt of ethylxanthate, and substituted pyridine. About 20 mL solution of cupric chloride dihydrate (0.0025 mole) in acetone was prepared. To this solution, a solution of potassium salt of ethyl xanthate (0.005 mole) and substituted

SCHEME 1: Scheme of the proposed structure, where $X = \begin{matrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{matrix}$.

TABLE 1: Molar conductance, magnetic moments, and analytical data of 1 : 1 adducts of bis(*O*-ethyldithiocarbonato)copper(II) with substituted pyridines.

S. No.	Name of the compound	Molar conductance (ohm ⁻¹ mol ⁻¹ cm ²)	μ_{eff} (B.M.) at 293 K	% found				% calculated			
				C	H	N	S	C	H	N	S
1	Bis(ethylxanthato)(2-methylpyridine)copper(II)	3.49	1.88	33.0	3.02	3.0	32.7	34.4	3.91	3.64	33.3
2	Bis(ethylxanthato)(3-methylpyridine)copper(II)	3.85	1.92	34.8	3.98	2.78	31.9	36.2	4.27	3.51	32.2
3	Bis(ethylxanthato)(4-methylpyridine)copper(II)	4.35	1.93	35.5	3.55	2.98	30.8	36.2	4.27	3.51	32.2
4	Bis(ethylxanthato)(2-ethylpyridine)copper(II)	3.89	1.76	36.6	4.01	3.15	30.7	37.9	4.61	3.40	31.1
5	Bis(ethylxanthato)(3-ethylpyridine)copper(II)	3.97	1.82	36.2	4.00	3.32	30.6	37.9	4.61	3.40	31.1
6	Bis(ethylxanthato)(4-ethylpyridine)copper(II)	4.74	1.85	36.6	3.98	3.20	30.2	37.9	4.61	3.40	31.1

pyridine (0.0025 mole) [2-methylpyridine = 0.235 g, 3-methylpyridine = 0.235 g, 4-methylpyridine = 0.235 g, 2-ethylpyridine = 0.27 g, and 3-ethylpyridine = 0.27 g, 4-ethylpyridine = 0.27 g] prepared in 50 mL of acetone was added slowly with constant stirring. Dark green coloured precipitates so obtained were filtered, washed with acetone, and dried over anhydrous calcium chloride in a vacuum desiccator at room temperature. A scheme of the proposed structure is shown in Scheme 1.

3. Results and Discussion

The addition complexes of bis(*O*-ethyldithiocarbonato)copper(II) are microcrystalline solids which are light green in colour. These are insoluble in common organic solvents such as ethanol, acetone, and benzene. However, these are soluble in dimethylformamide and dimethylsulfoxide. On the basis of elemental analysis (Table 1) they have been assigned the general formula $\text{Cu}(\text{S}_2\text{COC}_2\text{H}_5)_2\text{L}$ [L = 2-, 3-, 4-methyl and 2-, 3-, 4-ethyl-pyridines]. Conductance values of these complexes in DMF fall in the range of 3.50–5.00 ohm⁻¹ mole⁻¹ cm² (Table 1). These values are lower than the values expected for any uni-univalent electrolytes in this solvent suggesting that these complexes are neutral and nonionic in character [6, 7]. The magnetic moments of 1:1 complexes of bis(*O*-ethyldithiocarbonato)copper(II) with substituted pyridines fall in the range 1.81–1.94 B.M (Table 1) which is in agreement with magnetic moment values observed for distorted square pyramidal complexes of copper(II) [8–10].

Free dithiocarbonate shows vibrations due to C–O–C stretching in the range of 1270–1280 cm⁻¹ and the C–S

stretching vibration appears as two bands in the range of 1057–1070 cm⁻¹. In the present work, a single sharp band of high intensity has been observed in all the complexes in the range of 1011–1035 cm⁻¹ (Table 2). The appearance of the only C–S band suggests symmetrical bidentate binding of the dithiocarbonate moiety. There is a positive shift of 10–30 cm⁻¹ in comparison to the free ligands. This indicates that the dithiocarbonate ligand coordinates with the metal through sulfur atoms. Moreover, the complexes show a band in the region 1190–1220 cm⁻¹ which is attributed to ν (C–O) of dithiocarbonate moiety. In these complexes C–H out of plane bands occur at lower energy positions on complexation, indicating red shifts, which confirm that these ligands interact with the metal ion through their respective ring nitrogen atom. A new band of medium to strong intensity, observed in the range of 320–352 cm⁻¹, may be attributed to Cu–S stretching mode [11]. The electronic spectra of 1:1 addition complexes of bis(*O*-ethyldithiocarbonato)copper(II) have been recorded in DMF. The copper(II) five coordinate complexes are expected to show a strong broad band appearing in the region 12000–17500 cm⁻¹ (Table 2). The band maximum appears around 16000 cm⁻¹ and is assigned to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition. A weak shoulder is associated with it due to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. Third possible transition is orbitally forbidden and merges with the broad band. The relative energy order of these transitions depends upon the extent of axial ligand-metal interaction.

The complexes under observation show an intense band in the range of 15500–17500 cm⁻¹ which is attributed to d-d transitions as observed in most of the copper complexes (ν_1). This main absorption band around 16000 cm⁻¹ can be assigned to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (Table 2). The appearance of

TABLE 2: Electronic and vibrational spectral data of 1 : 1 adducts of bis(O-ethylthiocarbonato)copper(II) with substituted pyridines.

S. No.	Name of the adduct	Yield and (melting point)	ν_1 (cm ⁻¹)	ν (C-S)	ν (C-O)	ν (Cu-S)
1	Bis(ethylxanthato)(2-methylpyridine)copper(II)	62% (89°C)	16421	1012	1199	324
2	Bis(ethylxanthato)(3-methylpyridine)copper(II)	68% (87°C)	16623	1022	1210	335
3	Bis(ethylxanthato)(4-methylpyridine)copper(II)	70% (88.5°C)	16858	1032	1200	330
4	Bis(ethylxanthato)(2-ethylpyridine)copper(II)	65% (86.2°C)	16990	1020	1202	327
5	Bis(ethylxanthato)(3-ethylpyridine)copper(II)	68% (86.8°C)	16400	1034	1198	324
6	Bis(ethylxanthato)(4-ethylpyridine)copper(II)	69% (87.4°C)	15890	1037	1200	338

(a)

(b)

FIGURE 1

one band with the intensity pattern suggests square pyramidal geometry around copper(II) ion in these 1:1 adducts [12] Figure 1.

4. Conclusion

The results obtained from various physicochemical and spectral techniques suggest that the adducts of bis(*O*-ethyl-dithiocarbonato)copper(II) with substituted pyridines have 1:1 stoichiometry with square pyramidal geometry around copper(II) ion.

References

- [1] J. J. Santana and R. M. Souto, *Honolulu PRiME the Electrochemical Society*, 2012.
- [2] W. Mellert, E. Amtmann, V. Erfle, and G. Sauer, "Inhibition of HIV-1 replication by an antiviral xanthate compound in vitro," *AIDS Research and Human Retroviruses*, vol. 4, no. 1, pp. 71–81, 1988.
- [3] G. R. R. Behbehani, M. Mehreshtiagh, and L. B. A. A. Saboury, "A calorimetric investigation for the bindings of mushroom tyrosinase to p-phenylene-bis dithiocarbamate and xanthates," *Journal of the Serbian Chemical Society*, vol. 78, no. 2, pp. 255–263, 2013.
- [4] A. O. Görgülü, H. Çelikkan, and M. Arslan, "The synthesis, characterization and electrochemical behavior of transition metal complexes containing nitrogen heterocyclic sulphur donor ligand," *Acta Chimica Slovenica*, vol. 56, pp. 334–339, 2009.
- [5] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, *Vogel's Text Book of Practical Organic Chemistry*, Pearson Education, London, UK, 5th edition, 1989.
- [6] R. L. Martin and A. Whitley, "Magnetic studies with copper(II) salts. Part III. The constitution of copper(II)-alkanoates in solution," *Journal of the Chemical Society*, vol. 13, pp. 1394–1402, 1958.
- [7] W. J. Geary, "The use of conductivity measurements in organic solvents for the characterisation of coordination compounds," *Coordination Chemistry Reviews*, vol. 7, no. 1, pp. 81–122, 1971.
- [8] R. A. Ahmadi, F. Hasanvand, G. Bruno, H. A. Rudbari, and S. Amani, "Synthesis, spectroscopy, and magnetic characterization of Copper(II) and Cobalt(II) complexes with 2-Amino-5-bromopyridine as ligand," *ISRN Inorganic Chemistry*, vol. 2013, Article ID 426712, 7 pages, 2013.
- [9] L. Singh, D. K. Sharma, U. Singh, and A. Kumar, "Synthesis and spectral studies of Cu(II) coordination compounds of 4[N-(cinnamalidene) amino] antipyrine semicarbazone," *Asian Journal of Chemistry*, vol. 16, no. 2, pp. 577–580, 2004.
- [10] N. H. Al-Shaalan, "Synthesis, characterization and biological activities of Cu(II), Co(II), Mn(II), Fe(II), and UO₂(VI) complexes with a new Schiff base hydrazone: O-hydroxyacetophenone-7-chloro-4-quinoline hydrazone," *Molecules*, vol. 16, no. 10, pp. 8629–8645, 2011.
- [11] N. Singh and A. Parsad, "Synthesis, characterization and electrical conductivities of mixed-ligand (N, S/Se) heterobimetallic coordination polymers and their I₂-doped products," *Indian Journal of Chemistry A*, vol. 47, pp. 650–656, 2008.
- [12] M. Zhou, L. Song, and K. Shu, "A square-pyramidal copper(II) complex with strong intramolecular hydrogen bonds:

diaqua(*N,N'*-dimethylformamide- κ O)bis[2-(diphenylphosphoryl)benzoato- κ O]copper(II)," *Acta Crystallographica C*, vol. 69, pp. 463–466, 2013.