ORIGINAL PAPER

Synthesis and Characterization of the Adducts of Bis (O-butyldithiocarbonato)nickel(II) with Substituted Heterocyclic Amines and X-ray Structure of Bis(O-butyldithiocarbonato)bis (4-cyanopyridine)nickel(II)

Sanjay Kapoor · Renu Sachar · Kuldeep Singh · Vivek K. Gupta · Verma Rajnikant

Received: 24 June 2011/Accepted: 17 November 2011/Published online: 4 December 2011 © Springer Science+Business Media, LLC 2011

Abstract We report the synthesis and study of a new series of the adducts of Bis(O-butyldithiocarbonato)nickel(II) with substituted heterocyclic amines such as amino and cyanopyridines. Analytical results show that the adducts have 1:2 stoichiometry with general formula $M(Xan)_2L_2$ (M = Ni(II), Xan = O-butyldithiocarbonate, L = 2-, 3- and 4-aminopyridines, 3- and 4-cyanopyridines). The complexes have been characterized by analytical, magnetic susceptibility measurements, molar conductivity measurements, IR, electronic spectral data and X-ray diffraction analysis. One of the adducts, bis(O-butyldithiocarbonato)bis(4-cyanopyridine)nickel(II), crystallizes in the monoclinic space group P2₁/c with unit cell parameters : a = 12.546(4), b = 11.495(3),c = 9.351(3) Å, $\beta = 102.73(3)^{\circ}$, Z = 2. Crystal structure was solved by direct methods and refined by full matrix least squares procedures to a final R-value of 0.0299 for 2,788 observed reflections. The packing of layers of molecules is stabilized by weak C–H…N and C–H… π hydrogen bonds.

Keywords Adducts \cdot *O*-alkyldithiocarbonates (Xanthates) and substituted heterocyclic amines \cdot Direct methods \cdot Crystal structure \cdot C–H…N and C–H… π hydrogen bonding

Electronic supplementary material The online version of this article (doi:10.1007/s10870-011-0228-y) contains supplementary material, which is available to authorized users.

S. Kapoor · R. Sachar Department of Chemistry, University of Jammu, Jammu Tawi 180 006, India

K. Singh · V. K. Gupta · V. Rajnikant (⊠) X-ray Crystallography Laboratory, Post Graduate Department of Physics, University of Jammu, Jammu Tawi 180 006, India e-mail: rkvk.paper11@gmail.com

Introduction

O-alkyldithiocarbonates, popularly known as xanthates, are generally obtained by the reaction of an alcohol with CS_2 in the presence of KOH or NaOH. Xanthates are used in curing and vulcanization of rubber, as collectors of sulphide ores or minerals in froth-floatation process, as fungicides in agriculture and in the manufacture of synthetic textiles [1-5]. Metal xanthate complexes and their reaction products with a variety of Lewis bases have been extensively studied [6-8]. The soluble alkali metal xanthates are widely used in extraction and separation of Hg, Ag, Cd etc., [9-11]. Sodium and potassium ethyl xanthate have antidotal effects in acute mercury poisoning. Transition metal xanthate complexes have been investigated for non linear optical applications [12]. To the best of our knowledge, the reaction products of Ni(II) xanthate with substituted heterocyclic amines (Lewis bases) have been much less extensively studied than other similar compounds. In this article, we report the synthesis and investigation of the 1:2 adducts of bis(O-butyldithiocarbonato)nickel(II) with substituted heterocyclic amines such as 2-, 3- and 4-aminopyridines and 3- and 4-cyanopyridines. The X-ray crystal structure of $[Ni(C_6H_4N_2)_2]$ $(S_2CO-n-C_4H_9)_2$] i.e. Bis(O-butyldithiocarbonato)bis(4cyanopyridine)nickel(II) is also reported in this paper.

Experimental

Preparation of Potassium Salt of *O*-Butyldithiocarbonate

The potassium salt of O-butyldithiocarbonate was prepared by the standard published method [13]. 42 g (0.75 mol) of KOH Pellets were placed in a 500 mL flask and 193 g (238 mL) of butan-1-ol was added. The resulting solution was heated under reflux for 1 h and then allowed to cool. From the reaction mixture liquid portion was carefully decanted off. The residual solid was transferred into a dry 500 mL flask to which 57 g (45 mL, 0.75 mol) of CS₂ was added slowly with constant shaking. The resulting solid yellow mass was filtered after cooling in ice on a sintered glass funnel at the pump and it was washed with three 25 mL portions of ether. The potassium *O*-butylditiocarbonate obtained was dried in a vacuum dessicator over silica gel.

Preparation of bis(O-butyldithiocarbonato)nickel(II)

The complex bis(*O*-butyldithiocarbonato)nickel(II) was prepared by mixing and constant stirring of the aqueous solution of nickel(II) chloride (2.36 g, 0.01 mol) and potassium salt of *O*-butyldithiocarbonate (3.7 g, 0.02 mol). Green precipitates were formed which were filtered immediately and dried in a vacuum dessicator over anhydrous calcium chloride. The composition of the complex was established to be $[Ni(S_2COC_4H_9)_2]$ by the elemental analysis. Found (Calc.) C = 33.25(33.64), H = 4.89(5.04), S = 35.52 (35.88), Ni = 16.21 (16.45).

Preparation of the Adducts of bis (*O*-butyldithiocarbonato)nickel(II) with Substituted Heterocyclic Amines (substituted pyridines)

The 1:2 addition complexes of nickel(II)butylxanthate with substituted pyridines were prepared by stirring [Ni(S₂CO-n-C₄H₉)₂] (0.92 g, 0.0026 mol) in acetone with substituted pyridines [2-aminopyridine = 0.488 g, 3-aminopyridine = 0.488 g, 4-aminopyridine = 0.488 g, 3-cyanopyridine = 0.541 g and 4-cyanopyridine = 0.541 g (0.0052 mol)] for 30 min. The resulting solutions were concentrated by distillation to obtain the maximum yield. The contents of the reaction mixture were allowed to stand for 20–24 h and the green crystalline solid obtained was washed with the solvent used in their preparation and dried over calcium chloride at room temperature.

X-Ray Structure Determination

The X-ray intensity data for one of the compounds Bis-(*O*-butyldithiocarbonato)bis(4-cyanopyridine)nickel(II), were collected by using X'Calibur OXFORD DIFFRACTION system (now varian) with graphite monochromatic MoK α radiation ($\lambda = 0.71073$ Å). Data collection, reduction and correction for title compound was achieved using the CrysAlis^{Pro} software. The structure was solved by SHEL-XS-97 and refined with SHELXL-97 [14, 15]. The structure converged to a final *R*-value of 0.0299.

Methods

Carbon, Hydrogen, Nitrogen and Sulfur were determined on elemental analyzer (elemental vario EL III, carlo Erba 1108). Molar conductance was determined on the millimolar solution in DMF using century CC 601 Conductivity Bridge. Infrared spectra of the complexes over the region 4,000–200 cm⁻¹ were recorded using KBr pellets on Infrared spectrophotometer (Perkin Elmer FT-IR). The electronic spectra of the adducts were recorded in DMF on systronics 119 UV–visible spectrophotometer. Magnetic moments were determined at room temperature by VSM method (Princeton Applied Research-Model No. 155). The analytical data, molar conductance and magnetic moments of the adducts isolated are presented in Table 1S. Important IR bands and electronic spectral data are cited in Table 2S.

Results and Discussion

The complexes of bis(O-butyldithiocarbonato)nickel(II) with amino- and cyanopyridines are crystalline solids which are dark green or blackish-green. These adducts are soluble in common organic solvents such as acetone, chloroform, dimethylformamide and dimethylsulphoxide. The complexes obtained in this study gave analytical results which are concordant with the formulas assigned, as summarized in Table 1S. On the basis of elemental analysis (Table 1S) the adducts isolated having 1:2 stoichiometry are assigned the formula Ni(S₂COCH₂CH₂CH₂CH₃)₂ L_2 (where L = 2-, 3- and 4-aminopyridines, 3- and 4-cyanopyridines). The molar conductivity values calculated (in the range of 18.96-33.75 ohm⁻¹ mol⁻¹ cm²) from the conductivities measured on millimolar solutions of the adducts Ni(S2- $COCH_2CH_2CH_2CH_3)_2L_2$ in DMF, support the neutral and non-ionic nature of the complexes [16, 17]. The 1:2 adducts of bis(O-butyldithiocarbonato)nickel(II) with amino- and cyanopyridines exhibit magnetic moment in the range of 2.98-3.21 BM which is in agreement with magnetic moment values observed for octahedral complexes of nickel(II) [18, 19]. A comparison of the infrared spectra of the present complexes with those of the corresponding free ligands reveals that most of the absorption bands of free ligands are shifted in their respective complexes. Amino and cyanopyridines have two possible coordinating cites. It has been established that N-H and C-N frequencies must show red shift if the coordination occurs through amino group or cyano group nitrogen atom. But in the present complexes, they show, no appreciable red shift. Thus the possibility of coordination of 2-, 3- and 4-aminopyridines, 3- and 4-cyanopyridines through their amino or cyano nitrogen atom with metal is ruled out. This has been further confirmed by examining the C-H out of plane deformation

vibrations. In amino- and cyanopyridine complexes C–H out of the 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. The electronic spectra of 1:2 adducts of bis(*O*-butyldithiocarbonato)nickel(II) have been recorded in DMF. It shows three broad bands v_1 , v_2 and v_3 around 10,000, 18,000 and 28,000 cm⁻¹, respectively. These bands can be assigned due to, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ transitions, respectively. Appearance of these three broad bands along with shoulders show that adducts are having trans octahedral geometry around nickel (II) metal ion [20].

X-ray Crystallographic Studies

The crystallography data for bis(*O*-butyldithiocarbonato)bis(4-cyanopyridine)nickel(II) are presented in Table 1. Selected bond distances and bond angles for non- hydrogen atoms are listed in Table 3S. A general view of the molecule indicating atom numbering scheme is shown in Fig. 1. *Ortep-3 for Windows* [21] software was used for making the thermal ellipsoids. The geometry of the molecule was calculated using *PLATON* [22] and PARST [23] software.

In this compound the nickel (II) cation lies on an inversion centre. The asymmetric unit comprises of half molecule. The Ni(1)–N1 bond length is 2.127(1) Å while the Ni(1)–S1 and Ni(1)–S2 bond lengths are 2.429(4) and 2.444(4) Å, respectively. The two sulphur–carbon distances have almost identical values, since the nature of the double bond inside the four atom moiety is resonating. The six bond lengths in the pyridine ring lie in the range 1.334(2)–1.384(2) Å; average value being 1.365(2) Å.

The bond angles in the pyridine ring vary from 118.05(2) to 123.27(2)°, the average value being 119.96(7)°. The pyridine ring (N1, C2, C3, C4, C5, C6) is perfectly *planar* with a maximum deviation of 0.010(2) Å (observed for atom C3). The cyano group bound to C4 is significantly out of the plane of the phenyl ring as the torsion angle C5–C4–C7–N2 = $26(5)^\circ$. Out-of-plane position of the cyanide group is also evident from the least-squares plane calculation of the pyridine ring where the C7 and N2 atoms have been deviated below the pyridine ring (deviations for both the atoms being -0.084(2) and -0.166(2) Å, respectively).

The bond angles N1–Ni(1)–S1 and S1–Ni(1)–S2 with respect to nickel as the nodal or pivotal atom exhibit different values; the values being 91.10(4) and 74.26(1)°, respectively. The difference in these values is understandable as there is a significant stretch at Ni(1) as well as at C8 position. Both these positions are asymmetrically

Table 1 Crystal and experimental data

| CCDC No | 818905 |
|-------------------------------------------|---------------------------------------------------|
| Crystal description | Hexagonal plate greenish |
| Crystal size | $0.30 \times 0.30 \times 0.15 \text{ mm}^3$ |
| Melting point | 120 °C |
| Empirical formula | $C_{22}H_{26}N_4S_4O_2N_1$ |
| Formula weight | 282.71 |
| Measurement | X'Calibur System (now varian) |
| Radiation, Wavelength | MoK\α, 0.71073 Å |
| Unit cell dimensions | a = 12.546(4) Å |
| | b = 11.495(3) Å |
| | c = 9.351(3) Å |
| | $\beta = 102.73(3)^{\circ}$ |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /c |
| Unit cell volume | 1315.58(7) Å ³ |
| Density (calculated) | 1.427 mg/m^3 |
| Temperature | 293(2) K |
| Absorption coefficient | 1.081 mm^{-1} |
| <i>F</i> (000) | 588 |
| Scan mode | ω scan |
| θ range for entire data collection | $3.54^\circ < \theta < 28.00^\circ$ |
| Range of indices | -16 < h < 7, -15 < k < 11 |
| | -12 < l < 12 |
| Reflections collected/unique | 6320/3148 |
| R _{int} | 0.0204 |
| R _{sigma} | 0.0323 |
| Structure determination | Direct methods |
| Refinement | Full matrix least squares on F^2 |
| Weighing scheme | $[\Lambda\sigma^2(Fo^2) + (0.0467P)^2 + 0.0883P]$ |
| | where $P = (Fo^2 + 2Fc^2)/3$ |
| No. of parameters refined | 203 |
| Final R | 0.0299 |
| $wR(F^2)$ | 0.0781 |
| Goodness-of-fit | 1.003 |
| $(\Delta/\sigma)_{\rm max}$ | -0.001 for yH112 |
| Final residual electron density | $-0.484 < \Delta \rho < 0.055 \text{ eÅ}^{-3}$ |
| | |

loaded with pyridine ring and butyldithiocarbonato groups and hence give rise to stretching. The dithiocarbanato group exhibits a non-linear character. It is evident from the value of bond angles with respect to atom O1 [119.47(1)], C9 [107.02(1)], C10 [113.83(2)] and C11 [112.90(2)°], respectively. The amount of torsion present along N1– Ni(1) bond [-52.03(1) and $-53.78(1)^\circ$, respectively] is quite substantial. It indicates that the cyanopyridine group and dithiocarbonato groups are puckered along this bond. The cyanide group is significantly deviated from the plane of pyridine moiety (the deviation for C7 and N2 being -0.084(2) and -0.166(2) Å, respectively).



Fig. 1 ORTEP view of the molecule with displacement ellipsoids drawn at 50% probability level. H atoms are shown as small spheres of arbitrary radii

The dihedral angle between the least-squares plane of dithio-group (Ni(1), S1, C8, S2) and the pyridine ring is $88.53(3)^{\circ}$ meaning thereby that both these units are held almost perpendicular to each other. The dihedral angle between the dithio group and carbonato group is $38.29(7)^{\circ}$. Packing of the molecules in the unit cell down *b*-axis is shown in Fig. 2. Molecules are arranged in a manner to



Fig. 2 Packing diagram viewed down the b-axis

form layers. Molecules within the layers are parallel to each other. The nickel atom is located at each corner of the unit cell. The packing of molecular layers are stabilized by weak C-H···N and C-H··· π hydrogen bonds. Details of C-H···N and C-H··· π interaction are presented in Table 4S.

Conclusions

The various investigations like analytical data, conductivity measurement, spectral and magnetic studies done on the adducts reported in this article reveal that these adducts are octahedral, non-electrolytic and paramagnetic in nature.

Supplementary Material

CCDC no. 818905 contain the supplementary crystallographic data for the compound bis(O-butyldithiocarbonato)bis(4-cyanopyridine)nickel(II). The data can be obtained from free of charge via www.ccdc.cam.ac.uk/data_request/ cif by e-mailing data_request @ ccdc.cam.ac.uk.

Acknowledgments We are grateful to Institute Instrumentation Centre (IIC), Indian Institute of Technology, Roorkee for magnetic studies. One of the Authors (Rajnikant) acknowledges the Department of Science & Technology for single crystal X-ray diffractometer sanctioned as a National Facility under research project No. SR/S2/CMP-47/2003.

References

- 1. Gimeno MC, Jambrina E, Laguna A, Murray HH, Terroba R (1996) Inorg Chem Acta 249:69
- 2. Allen FH, Kennard O (1993) Chem Des Autom News 8:31
- 3. Victorriano LI, Cortes HB (1996) J Coord Chem 39:231
- Rao SR (1971) Xanthates and related compounds. MDekker, New York
- 5. Ara I, Behij FE (2003) Trans Met Chem 28:908
- 6. Litipova Sh Z, Khakimova VK, Tukhtaev S (1991) Uzb Khim Zh 2:3
- 7. Xiong RG, Yu Zh, Liu CM, You XZ (1997) Polyhedron 16:2667
- 8. Gable RW, Hoskins BF, Winter G (1985) Inorg Chem Acta 96:151
- 9. Reddy PCh, Rangamannar B (1996) J Radional Nucl Chem 213:9
- PCh Reddy, Rangamannar B (1996) J Radioanal Nucl Chem 214:159
- 11. Wolf N, Roundhill DM (1994) Polyhedron 13:2801
- Zelmon DE, Gebeyhu Z, Tomlin DC, Thomas M (1998) Mater Res Symp Proc 519:395
- Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR (1989) Vogel's text book of practical organic chemistry, 5th edn. Pearson Education, London
- 14. Sheldrick GM, SHELXS97 (1997) Program for the solution of crystal structures. University of Gottingen, Gottingen
- Sheldrick GM, SHELXL97 (1997) Program for the refinement of crystal structures. University of Gottingen, Gottingen

- 16. Martin RL, Whitley A (1958) J Chem Soc 1394
- 17. Lever ABP (1965) J Inorg Nucl Chem 27:149
- 18. Basolo F, Matousch WR (1953) J Am Chem Soc 75:5663
- 19. Coucouvanis D, Fackler JP (1967) Inorg Chem 6:2047
- 20. Lever ABP (1984) Inorganic electronic spectroscopy. Elsevier, Amsterdam
- 21. Farrugia LJ (1997) J Appl Cryst 30:565
- 22. Spek AL (1999) PLATON for windows version. University of Utrecht, Utrecht
- 23. Nardelli M (1995) J Appl Cryst 28:659