



X-RAY CRYSTALLOGRAPHY OF BIS(*O*-ETHYLXANTHATO)- BIS(3,5-DIMETHYLPYRIDINE)NICKEL(II)

Kuldeep Singh,^[a] Gurpreet Kour,^[b] Ritu Sharma,^[b] Renu Sachar,^[b] Vivek K. Gupta,^[a] Rajni Kant^{[a]*}

Keywords: Octahedral coordination, direct methods, crystal structure; bis(*O*-ethylxanthato)bis(3,5-dimethylpyridine)nickel(II)

A six-coordinated Ni(II) complex, bis(*O*-ethylxanthato)bis(3,5-dimethylpyridine)nickel(II), [C₂₀H₂₈N₂NiO₂S₄], has been synthesized by the reaction of bis(*O*-ethylxanthato)nickel(II) with 3,5-dimethylpyridine in acetone. The Ni atom in the title complex is octahedrally coordinated within a trans-N₂S₄ donor set, with the Ni atom located on a centre of inversion. The structure of the title compound was elucidated by a single-crystal X-ray diffraction method. The compound crystallizes in the triclinic space group *P*-1 with unit-cell parameters: *a* = 7.1750(3) Å, *b* = 9.3864(5) Å, *c* = 9.6914(4) Å and $\alpha = 84.962(4)^\circ$, $\beta = 73.017(4)^\circ$, $\gamma = 75.172(4)^\circ$. The crystal structure was solved by direct methods and refined by full-matrix least-squares procedures to a final *R*-value of 0.0238 for 2162 observed reflections. The asymmetric unit comprises half a molecule. The pyridine ring is coplanar, and is held almost perpendicular to the dithiocarbonato group. Molecules in the crystal are packed together to form layers.

* Corresponding Authors

Fax: +91 191 243 2051

E-Mail: rkvk.paper11@gmail.com

[a] X-ray Crystallography Laboratory, Post-Graduate
Department of Physics & Electronics,

University of Jammu, Jammu Tawi - 180 006, India

[b] Department of Chemistry, University of Jammu, Jammu
Tawi-180 006, India

Introduction

Xanthates comprise an important class of 1,1-dithiolate ligands with many applications ranging from flotation agents to rubber vulcanizers.¹ Bivalent metal xanthates are known to form stable adducts with nitrogen donors which exhibit a variety of coordination geometries.² Metal xanthates are extensively used as pharmaceuticals, fungicides, pesticides, rubber accelerators, corrosion inhibitors, agricultural reagents and quite recently in therapy for HIV infections.^{3,4} They form a chelate with virtually all transition elements, and has proved to be a versatile chelating agent for the separation and extraction of metals in analytical chemistry and mineral flotation.⁵ Coordination complexes of xanthato ligands with a variety of transition as well as non-transition metals have been reported.^{6,7} As a part of our continuous research in this area, the title complex was prepared in the crystalline form and its various geometrical parameters were investigated.

Experimental Methods

Synthesis

Potassium *O*-ethylxanthate is prepared by reacting potassium hydroxide, carbon disulfide and ethyl alcohol according to the method available in the literature.⁸ The complex bis(*O*-ethylxanthato)nickel(II) was prepared by stirring an aqueous solution of nickel(II)chloride (2.37 g, 0.01 mol) and potassium *O*-ethylxanthate (3.2g, 0.02mol).

Green precipitates of bis(*O*-ethylxanthato)nickel(II) were obtained which were filtered and dried in a vacuum desiccator. A solution of bis(*O*-ethylxanthato)nickel(II) (0.78 g, 0.0026 mol) in 50 mL of acetone was treated with excess of 3,5-dimethylpyridine and stirred for 30 min. The colour of the reaction mixture changed from brown to green. After allowing the solution to stand overnight at room temperature, bright green crystals of bis(*O*-ethylxanthato)bis(3,5-dimethylpyridine)nickel(II) were obtained.

X-ray Data Collection, Crystal Structure Determination and Refinement

X-ray intensity data of 14136 reflections (of which 2367 unique) were collected on a CCD area-detector diffractometer (*X'calibur system-Oxford diffraction make, U.K.*) which is equipped with graphite monochromated MoK α radiation ($\lambda=0.71073$ Å). The crystal used for data collection was of dimensions 0.3 x 0.2 x 0.2 mm³. The cell dimensions were determined by least-squares fit of angular settings of 10746 reflections in the θ range 3.46 to 29.03°. The intensities were measured by ϕ and ω scan mode for θ ranges 3.47 to 26.00°. 2162 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for Lorentz and polarization factors. The structure was solved by direct methods using *SHELXS97* software.⁹ A total of 1024 phase sets were refined with the correct phase set having an absolute figure of merit, $M(\text{abs}) = 1.262$ and combined figure of merit $\text{CFOM} = 0.045$. Multisolution tangent refinement was carried out using 849 *E*-values with $E > 1.2$. An E-map drawn with the correct set of phases revealed all the non-hydrogen atoms of the molecule. The R-factor based on the 849 *E*-values was $R_E = 0.222$. Full-matrix least-square refinement of the structure was carried out with *SHELXL97* software.⁹ *Ortep-3 for Windows* software [10] was used for making the thermal ellipsoids.¹⁰ The geometry of the molecule was calculated using *PLATON*¹¹ and *PARST*¹² software. CCDC-953601 contains the

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and other experimental details for (I)

CCDC	953601
Chemical formula	C ₂₀ H ₂₈ N ₂ NiO ₂ S ₄
Formula weight	515.39
Temperature	293(2) K
Measurement	X'Calibur System (now varian)
Radiation, Wavelength	MoK α , 0.71073 Å
Unit cell dimensions	a = 7.1750(3) Å, b = 9.3864(5) Å, c = 9.6914(4) Å α = 84.962(4)°, β = 73.017(4)° γ = 75.172(4)°
Crystal system, Space group	P-1
Unit cell volume	603.38(5) Å ³
Density (calculated)	1.418 g cm ⁻³
Absorption coefficient	1.168 mm ⁻¹
F (000)	270
θ range for entire data collection	3.47 < θ < 26.00°
Range of indices	-8 < h < 8, -11 < k < 11, -11 < l < 11
Reflections collected / unique	14136/ 2367
Reflections observed ($I > 2\sigma(I)$)	2162
R_{int}	0.0269
R_{σ}	0.0156
Weighing scheme	$\lambda[\sigma^2(F_o^2) + (0.0316P)^2 + 0.2328P]$ where $P = (F_o^2 + 2F_c^2)/3$
No. of parameters refined	136
Final R	0.0238
WR(F^2)	0.0623
Goodness-of-fit	1.054
(Δ/σ) _{max}	0.001 for OSF
Final residual electron density	-0.168 < $\Delta\rho$ < 0.239 Å ⁻³

Table 2. Selected bond lengths (Å) and angles (°) for non-hydrogen atoms (e.s.d.'s are given in parentheses)

Bond lengths		Bond angles	
Ni1-N1	2.114(1)	N1-Ni1-S2	89.99(4)
Ni1-S2	2.4468(4)	N1-Ni1-S3	89.70(4)
Ni1-S3	2.4653(4)	S2-Ni1-S3	73.38(1)
S2-C8	1.683(2)	C8-S3-Ni1	82.39(6)
S3-C8	1.687(2)	C8-O1-C9	119.56(14)
O1-C8	1.333(2)	C8-S2-Ni1	83.04(6)
O1-C9	1.457(2)	C8-O1-C9	119.56(14)
N1-C1	1.331(2)		
N1-C5	1.335(2)		

Results and Discussion

A general view of the molecule indicating atom numbering scheme (thermal ellipsoids drawn at 40% probability level) is shown in Figure 1. *Ortep-3 for Windows* software¹⁰ was used for making the thermal ellipsoids. Crystal data, along with data collection and structure refinement details are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

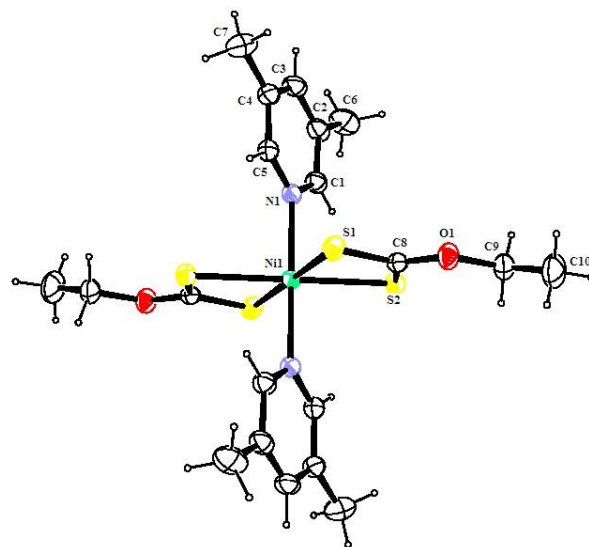
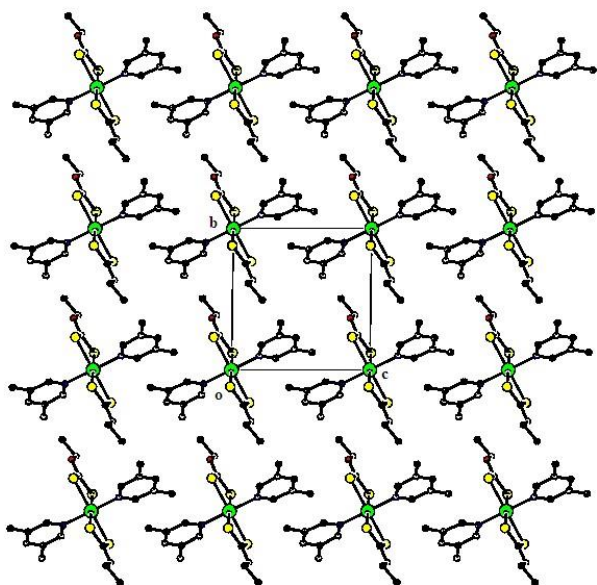


Figure 1. ORTEP view of the molecule with displacements ellipsoids drawn at 50% probability level. H atoms are shown as small spheres of arbitrary radii.

The asymmetric unit comprises of half molecule. The nickel atom is located at the inversion centre. The Ni(II) atom in the complex is six coordinated by two pyridine N atoms from two 2-dimethylpyridine ligands, and by four S atoms from two different xanthate ligands, exhibiting a distorted octahedral configuration of the Ni (II) atom.¹³ The Ni1-N1 bond length of 2.115(3) Å, and the Ni-S distances, which for Ni1-S2= 2.447(4) and Ni1-S3 = 2.465(4) Å are normal for this type of compound. The two sulphur-carbon distances show double bond character due to the delocalization over the two C-S bonds.¹⁴

The sulfur atoms and the Ni atom are lying in the same plane. The bond angle around the nickel atom are in the range of 73.38(4) to 180° and the bond angles in the pyridine ring vary from 117.1(2) to 123.5(2)°, the average value being 120.00(2)°. The pyridine ring (N1, C1, C2, C3, C4, C5) is perfectly *planar* with a maximum deviation of -0.003(2) Å (observed for atom C5). The two methyl groups bound to C2 and C4 atoms are lying in the same plane as that of pyridine ring and it is evident from the least-squares plane calculation of the pyridine ring where the deviation for

C6 and C7 atoms are marginal being -0.023(2) and 0.018(2) respectively. The O1-C8 bond distance [1.333(2) Å] is shorter than O1-C9 [1.457(2) Å] as a consequence of the hybridization of the carbon atom.¹⁵ By and large, the values for bond distances and angles are in agreement with related structures.¹⁶⁻¹⁸ The dihedral angle between the least-squares plane of dithio-group (Ni1, S1, C8, S2) and the pyridine ring is 89.58(4)° meaning thereby that both the units are held almost perpendicular to each other.



Figures 2. The crystal packing projected on the bc-plane

Packing of the molecules in the unit cell down b-axis is shown in Fig. 3. Molecules are arranged in a manner to form layers. Molecules within the layers are parallel to each other. The nickel atom is located at the each corner of the unit cell. In the absence of any significant hydrogen interaction, the packing of the molecule within the unit cell is stabilized with the help of Van der Waal forces.

Acknowledgements

One of the authors (Rajni Kant) acknowledges the Department of Science & Technology for single crystal X-ray diffractometer as a National Facility under Project No. SR/S2/CMP-47/2003.

References

- ¹ Tiekink, E. R. T., Haiduc, I., *Prog. Inorg. Chem.*, **2005**, *54*, 127.
- ² Jiang, X. H., Zhang, W. G., Zhong, Y., Wang, S.L. *Molecules*, **2002**, *7*, 549.
- ³ Victoriano, L. I., Cortes, H. B., *J. Coord. Chem.*, **1996**, *39*, 231.
- ⁴ Ara, I., Bahij, F.E., Lachkar, M., Larbi, N.B., *Trans.Met.Chem.*, **2003**, *28*, 908.
- ⁵ Wolf, N., Roundhill, D. M., *Polyhedron*, **1994**, *13*, 2801.
- ⁶ Travniecek, Z., Pastorek, R., Sindelar, Z., Marek, J., *J. Coord. Chem.*, **1998**, *44*, 193-204.
- ⁷ Ballester, L., Gutierrez, A., Perpignan, M. F., *Polyhedron*, **1996**, *15*, 1103.
- ⁸ Furnniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., *Vogel's textbook of Practical Organic Chemistry*, 5th Edn. Pearson Education, London, **1989**.
- ⁹ Sheldrick, G. M., *Acta Cryst.*, **2008**, *A64*, 112.
- ¹⁰ Farrugia, L. J., *J. Appl. Cryst.*, **2012**, *45*, 849.
- ¹¹ Spek, A. L., *Acta Cryst.*, **2009**, *D65*, 148.
- ¹² Nardelli, M., *J. Appl. Cryst.*, **1995**, *28*, 659.
- ¹³ Zhu, H. L., Shao, S. C., Ma, J. L., Qiu, X. Y., Sun, L., Yang, S., *Acta Cryst.*, **2003**, *E59*, m843.
- ¹⁴ Jiang, X. H., Zhang, W. G., Zhong, Y., Wang, S. L. *Molecules*, **2002**, *7*, 549.
- ¹⁵ Alam, N., Ehsan, M. A., Zeller, M., Mazhar, M., Arifin, Z. *Acta Cryst.*, **2011**, *E67*, m1064.
- ¹⁶ Kapoor, S., Sachar, R., Singh, K., Gupta, V. K., Rajnikant J. *Chem. Crystallogr.*, **2012**, *42*, 222.
- ¹⁷ Kapoor, S., Kour, R., Sachar, R., Kant, R., Gupta, V. K., Kapoor, K., *Acta Cryst.*, **2012**, *E68*, m58.
- ¹⁸ Singh, K., Kapoor, S., Sachar, R., Gupta, V. K., Rajnikant, *X-ray Struct Anal. Online*, **2012**, *28*, 43.

Received: 11.03.2014.

Accepted: 08.04.2014.