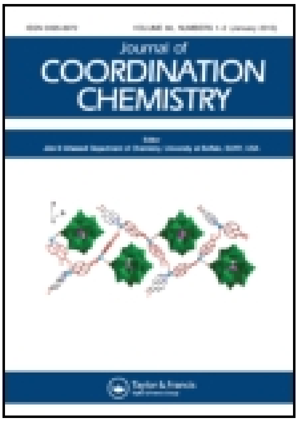
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:50
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

# A linear S-bridged trinuclear cobalt(III) complex with 2-aminobenzenethiol: synthesis, crystal structure, and spectroscopic characterization

Anangamohan Panja [a] [b] , Curtis E. Moore [c] & David M. Eichhorn [b]
[a] Postgraduate Department of Chemistry, Panskura Banamali College , Panskura RS, India
[b] Department of Chemistry , Wichita State University , Wichita , KS , USA
[c] Department of Chemistry and Biochemistry , University of California , San Diego, La Jolla , CA , USA
Accepted author version posted online: 11 Jul 2013.Published online: 02 Aug 2013.

To cite this article: Anangamohan Panja , Curtis E. Moore & David M. Eichhorn (2013) A linear S-bridged trinuclear cobalt(III) complex with 2-aminobenzenethiol: synthesis, crystal structure, and spectroscopic characterization, Journal of Coordination Chemistry, 66:17, 3037-3044, DOI: 10.1080/00958972.2013.823486

To link to this article: http://dx.doi.org/10.1080/00958972.2013.823486

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

*Journal of Coordination Chemistry*, 2013
Vol. 66, No. 17, 3037–3044, http://dx.doi.org/10.1080/00958972.2013.823486

# A linear S-bridged trinuclear cobalt(III) complex with 2-aminobenzenethiol: synthesis, crystal structure, and spectroscopic characterization

ANANGAMOHAN PANJA*†‡, CURTIS E. MOORE§ and DAVID M. EICHHORN*‡

†Postgraduate Department of Chemistry, Panskura Banamali College, Panskura RS, India
‡Department of Chemistry, Wichita State University, Wichita, KS, USA
§Department of Chemistry and Biochemistry, University of California, San Diego,
La Jolla, CA, USA

(*Received 20 June 2012; in final form 18 June 2013*)

Treatment of cobalt(II) perchlorate hexahydrate with 2 M equiv. of 2-aminobenzenethiol (Habt) in acetonitrile afforded a tricationic tricobalt complex, $[Co\{Co(abt)_3\}_2](ClO_4)_3\cdot2CH_3CN$, by aerial oxidation. The molecular structure of the meso (ΔΛ) form of the complex was determined by X-ray crystallography. In the complex cation, the central Co is coordinated by six thiolate groups from two terminal *fac*(*S*)-$[Co(abt)_3]$ units in an octahedral geometry, forming a linear S-bridged tricobalt structure.

*Keywords*: Trinuclear S-bridged linear Co(III) complex; 2-Aminobenzenethiol; Crystal structure of the meso isomer; Spectral properties

## 1. Introduction

The chemistry of metal-thiolate compounds has attracted attention because of their utility as structural and functional models for metal-cysteine centers in metalloenzymes [1, 2]. Over the last few years, we have been engaged in the synthesis of metal complexes containing mixed N–S donors [3–5]. Recently, we reported Co(III) complexes with $N_2S$, $N_3S_2$, and $N_2S_3$ donors in an effort to synthesize models for bacterial nitrile hydratase enzymes (NHase), which catalyze the partial hydration of nitriles to amides and which have noncorrinoid cobalt centers with mixed nitrogen/sulfur coordination environments [6, 7].

Chelating N–S donors have been used as ligands to transition metals for the better part of a century [8] and homoleptic metal complexes of both *o*-aminobenzenethiolate (abt) [9] and 2-aminoethanethiolate (aet) [10], including those of the form $ML_3$ for both L = abt and aet, have been known since the 1950’s. In addition, the ability of such $ML_3$ complexes to act as metalloligands to a central metal and form linear trinuclear species of the form $[M'(ML_3)_2]^{n+}$ has been known since the 1960’s [11, 12]. There are a number of structurally characterized examples of such species with L = aet (and closely related L = cysteinate)

---

*Corresponding authors. Email: ampanja@yahoo.co.in (A. Panja); david.eichhorn@wichita.edu (D.M. Eichhorn)

[13–29], however there are no structurally characterized examples of such complexes with L = abt. We report, herein, the synthesis and crystal structure of $[Co\{Co(abt)_3\}_2](ClO_4)_3$ – the first structurally characterized species of this class of complex incorporating *o*-aminobenzenethiolate ligands.

## 2. Experimental

### 2.1. *Materials and physical measurements*

All chemicals and solvents were of reagent grade and used as received from Aldrich, Acros, and Fisher Scientific without purification. Elemental analyses for C, H, and N were conducted using the Pregl–Dumas technique on a Thermo Fischer Flash EA1112. FTIR spectra were recorded from 400 to 4000 $cm^{-1}$ on a Nicolet 750 Magna-IR spectrometer using KBr pellets. UV–vis data were collected on a Hitachi U-2010 spectrophotometer. Conductivity measurements were made with a Systronics direct reading conductivity meter (model 304).

*Caution*! Perchlorate salts are potentially explosive and should be handled only in small quantities and with great care.

### 2.2. *Synthesis of $[Co\{Co(abt)_3\}_2](ClO_4)_3 \cdot 2CH_3CN$ (1)*

To a solution of 2-aminobenzenethiol (250 mg, 2.0 mM) in acetonitrile (10 mL) was added a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (366 mg, 1.0 mM) in acetonitrile (10 mL). The resulting brown solution was heated to reflux for 1 h during which a brown microcrystalline solid separated, which was then collected by filtration. The product was washed with acetonitrile and diethyl ether, and dried in air. Brown prismatic crystals suitable for X-ray crystallographic studies were obtained by slow evaporation from a solution of acetonitrile–methanol. Yield 360 mg (0.28 mM, 83%). Elemental Anal. Calcd for $C_{36}H_{36}Cl_3Co_3N_6O_{12}S_6 \cdot 1.9CH_3CN \cdot 0.4CH_3OH \cdot 0.3H_2O$: C, 36.69; H, 3.36; N, 8.41. Found: C, 36.69; H, 3.39; N, 8.42%. IR (KBr, $cm^{-1}$): 3214 m ($\nu_{NH}$); 3136, 3107 w ($\nu_{CH}$); 1600, 1558, 1449 m ($\nu_{C=C}$); 1088, 625 S ($\nu_{Cl–O}$). UV–vis (MeOH): $\lambda_{max}$ ($\varepsilon_M$, $M^{-1}\,cm^{-1}$) 324 (6063); 434 sh; 470 (5490); 595 sh.

### 2.3. *X-ray crystallography*

Single crystal X-ray diffraction data were collected using a Bruker Kappa ApexII diffractometer (Mo K$\alpha$, $\lambda = 0.71073$ Å) equipped with an Oxford Cryostream 700 low-temperature apparatus. A suitable single crystal of **1** was identified under a polarizing microscope and affixed with oil in a Hampton Research Cryoloop and transferred to the cold nitrogen stream of the diffractometer. The unit cell was determined from the setting angles of 36 frames of data. Several scans in $\varphi$ and $\omega$ directions were made to increase the number of redundant reflections and were averaged during refinement cycles. Data reduction was performed using the Bruker SAINT software package [30]. The structures were solved by direct methods and refined using full-matrix least-squares on $F^2$ (SHELXL-97) [31] within the OLEX2 structure solution package [32]. The intensity data were corrected for Lorentz and polarization effects, and all nonhydrogen atoms were refined using anisotropic thermal parameters. Hydrogens were placed at calculated positions, but were not refined. X-ray data collection and structure solution parameters for the complex are listed in table 1.

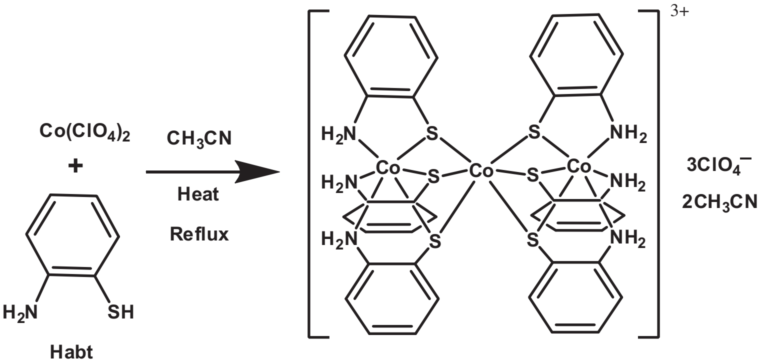
Table 1. Crystal data and structure refinement for $[Co\{Co(abt)_3\}_2](ClO_4)_3{\cdot}2CH_3CN$ (**1**).

| | |
|---|---|
| Empirical formula | $C_{36.80}H_{38.90}{\cdot}Cl_3O_{12}Co_3N_{6.30}S_6$ |
| Formula weight | 1249.74 |
| Temperature (K) | 150(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Rhombohedral |
| Space group | $R\bar{3}c$ |
| Unit cell dimensions (Å, °) | $a = 11.5120(4)$ $\alpha = 90$<br>$b = 11.5120(4)$ $\beta = 90$<br>$c = 67.054(2)$ $\gamma = 120$ |
| Volume ($Å^3$) | 7695.8(6) |
| $Z$ | 6 |
| Density (calculated) ($Mg/m^3$) | 1.618 |
| Absorption coefficient ($mm^{-1}$) | 1.422 |
| $F$ (000) | 3805 |
| $\theta$ range for data collection (°) | 1.82–26.00 |
| Index ranges | $-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-85 \leqslant l \leqslant 85$ |
| Reflections collected | 54,369 |
| Independent reflections | 1903 [$R_{(int)} = 0.0296$] |
| Completeness to $\theta = 26.00°$ (%) | 100.0 |
| Data/restraints/parameters | 1638/5/130 |
| Goodness of fit on $F^2$ | 1.075 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0342$, $wR_2 = 0.0892$ |
| $R$ indices (all data) | $R_1 = 0.0408$, $wR_2 = 0.1945$ |
| Largest diff. peak and hole (e $Å^{-3}$) | 0.459 and −0.545 |

## 3. Results and discussion

### 3.1. *Synthesis and structure of 1*

Previously reported syntheses of $[M'(ML_3)_2]^{3+}$ complexes have involved the synthesis and isolation of $ML_3$ followed by treatment of $ML_3$ with half an equivalent of a M′(III) salt or simply by treatment of $ML_3$ with acid (resulting in a complex in which M=M′). In our hands, **1** is synthesized directly by the reaction of $Co(ClO_4)_2$ with two equivalents of Habt (scheme 1), under aerobic oxidation which was responsible for the trivalent state of Co in the final product. The crystal structure of **1** shows $[Co\{Co(abt)_3\}_2]^{3+}$ along with three perchlorates and disordered water, methanol, and acetonitrile. The stoichiometry is in



$[Co\{Co(abt)_3\}_2](ClO_4)_3{\cdot}2MeCN$

Scheme 1. Synthetic route to **1**.

agreement with elemental analysis as well as the observed molar conductivity of $345\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$, which is consistent with a 1 : 3 electrolyte [14, 21, 23]. The central Co is situated at a position with $\bar{3}$ symmetry in the rhombohedral space group $R\bar{3}c$, with the 3-fold axis coincident with the Co–Co–Co vector. The perchlorate is situated on a 2-fold axis and has been modeled with two sets of oxygens present in a ratio of 86/14. Two solvent positions have been modeled, one with disordered water over a crystallographic 3-fold axis, with a total occupancy of 0.6 per Co trimer, and the other coincident with a 3-fold axis with occupancies of 0.6 methanol and 0.9 acetonitrile molecules per Co trimer. Both the crystal structure and the elemental analyses are best modeled with all three lattice solvents, although the relative abundance of the three solvents differs somewhat between the crystal and the bulk sample. For convenience, **1** is described as a bis(acetonitrile) solvate herein. A perspective drawing of the complex cation is shown in figure 1, and the selected bond distances and angles are listed in table 2.

The complex cation consists of three cobalts and six abt ligands. Each of the two terminal cobalts is chelated by three abt ligands to form a *fac*-(S)-[Co(abt)$_3$] unit with a $\text{CoN}_3\text{S}_3$ chromophore. The three sulfurs of each [Co(abt)$_3$] then serve as donors to the central Co (III). The symmetry imposed on the cation results in there being only one unique Co–N distance (2.004(2) Å) and two unique Co–S distances. The Co–S bond distances are in the range of analogous bond distances in $[\text{Co}\{\text{CoL}_3\}_2]^{3+}$ with L = aet [25–27] or cysteinate [27–29]. The Co–S bond distances within the two terminal *fac*-(S)-[Co(abt)$_3$] units ($\text{Co}_\text{t}$–S=2.2290(7) Å) are slightly shorter than those around the central Co ($\text{Co}_\text{c}$–S = 2.2712 (6) Å). This mirrors the situation in the published structures of analogous trinuclear species involving aet and cysteinate ligands. The Co–N bond distance, while not particularly long,

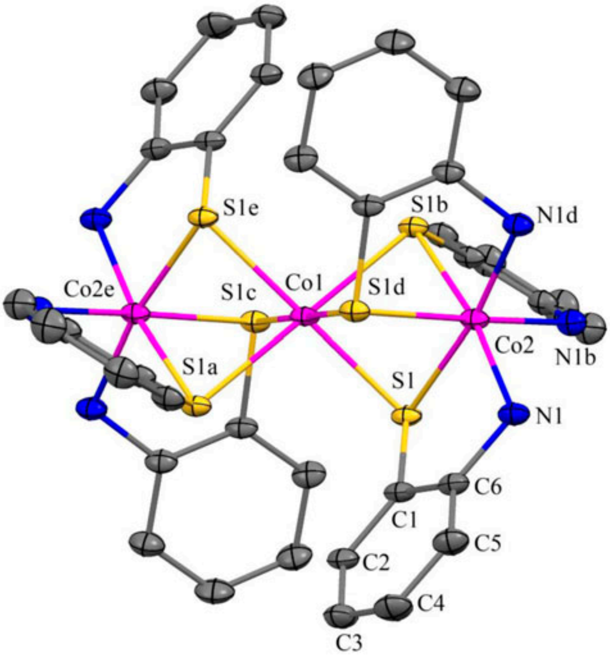


Figure 1. Molecular structure of $[\text{Co}\{\text{Co(abt)}_3\}_2](\text{ClO}_4)_3\cdot 2\text{CH}_3\text{CN}$; ellipsoids are drawn at 30% probability. Perchlorates, acetonitrile, and hydrogens are omitted for clarity. Symmetry code: $a = y-1, -x+y, -z$; $b = -y+1, x-y+2, z$; $c = x-y+1, x+1, -z$; $d = -x+y-1, -x+1, z$; $e = -x, -y+2, -z$.

Table 2. Selected bond distances (Å) and angles (°) for **1** and averages of analogous measurements for $[Co\{Co(aet)_3\}_2](SO_4)Cl$ [25].

| Bond/angle | **1** | $[Co\{Co(aet)_3\}_2]^{3+}$ | Bond/angle type |
|---|---|---|---|
| Co(2)–S(1) | 2.2712(6) | 2.262 | $Co_c$–S |
| Co(1)–S(1) | 2.2290(7) | 2.238 | $Co_t$–S |
| Co(1)–N(1) | 2.004(2) | 1.986 | $Co_t$–N |
| Co1···Co2 | 2.8622(7) | 2.857 | |
| S(1)–Co(2)–S(1)[a] | 97.11(2) | 97.43 | Across trimer |
| S(1)–Co(2)–S(1)[b] | 82.89(2) | 82.57 | Across trimer |
| N(1)–Co(1)–S(1)[b] | 170.90(7) | 173.16 | Interligand trans |
| N(1)–Co(1)–S(1) | 87.26(6) | 88.22 | Abt bite angle |
| S(1)–Co(1)–S(1)[b] | 84.83(3) | 84.5 | Same side of trimer |
| S(1)–Co(2)–S(1)[c] | 180.0 | 180.0 | Across trimer |
| S(1)–Co(1)–N(1)[b] | 89.98(7) | 92.76 | Interligand cis |
| N(1)–Co(1)–N(1)[b] | 97.25(9) | 94.6 | Interligand |

Symmetry transformations used to generate equivalent atoms: $a = y-1, -x+y, -z$; $b = -y+1, x-y+2, z$; $c = -x, -y+2, -z$.

is longer than that for the six $[Co\{CoL_3\}_2]^{3+}$ structures, in which the Co–N bond distances range from 1.984 to 2.004 Å. Other metrical parameters are also similar to those reported for $[Co\{Co(aet)_3\}_2]^{3+}$, as indicated in table 2. Deviation from ideal octahedral geometry within the terminal *fac*-(S)-$[Co(abt)_3]$ unit can be seen in the obtuse N–Co–N angles (97.25(9)°) and acute S–Co–S angles (84.83(3)°). Again, this is comparable to the deviations previously reported for analogous systems. Most importantly, several similar trinuclear metal complexes with aliphatic aminothiolate ligands such as 2-aminoethanethiolate and L-cysteinate are known, but **1** is the first-reported member of this class with the aromatic 2-aminobenzenethiolate.

As the molecule sits on an inversion center, the structure is necessarily the racemic meso isomer, with one terminal Co displaying Δ configuration and the other displaying Λ. The overall stereochemistry is best described as Δ(δδδ)Λ(λλλ), implying that the C–C bonds bridging S and N are parallel to the 3-fold axis (i.e. the Co–Co–Co vector). However, there is a significant deviation from the ideal geometry, which would require a 180° torsion angle involving the C–C bond and two Co atoms (C6–C1–Co1–Co2e). In the published structures involving aet and cysteinate, this angle is close to the ideal linear value, ranging from 170–180°. However, in **1**, this torsion angle is reduced to 146°, indicating the effect of the more rigid $sp^2$-hybridized carbons in abt. The molecular packing is stabilized by a complex network of hydrogen bonds, similar to that seen in $[Co\{Co(aet)_3\}_2](SO_4)Cl$ [25], in which each amine hydrogen is involved in a moderately strong hydrogen bond to perchlorate (table 3). This hydrogen bonding motif results in the cations and anions forming alternate layers parallel to the *ab* plane, as shown in figure 2.

Table 3. Hydrogen bonds (Å, °) between complex cation and perchlorate for $[Co\{Co(abt)_3\}_2](ClO_4)_3\cdot 2CH_3CN$.

| D–H···A | D···A | ∠D–H···A |
|---|---|---|
| N1–H1B···O1B[d] | 2.94(2) | 124(2) |
| N1–H1A···O2B[e] | 3.06(2) | 151(3) |
| N1–H1B···O1 | 3.008(4) | 179(3) |

Symmetry transformation used to generate equivalent atoms: $d = y+1/3, x-1/3, -z+1/6$; $e = x-y-2/3, -y-1/3, -z+1/6$.

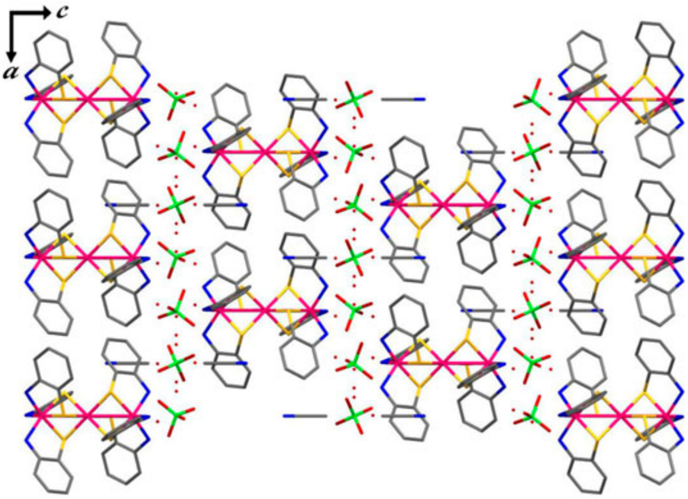


Figure 2. Molecular packing of $[Co\{Co(abt)_3\}_2](ClO_4)_3 \cdot 2CH_3CN$ viewed along the *b* axis. Hydrogens are omitted for clarity.

## 3.2. *Electronic spectroscopy*

The UV–visible spectrum (figure 3) of **1** is similar to that observed for similar S-bridged complexes. The lowest energy visible absorption at 595 nm can be assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition. However, assignment of bands in these complexes is complicated by overlap of transitions from two chromophores – the terminal $Co(III)N_3S_3$ and the central $Co(III)S_6$ [12]. The higher energy absorption bands observed for the

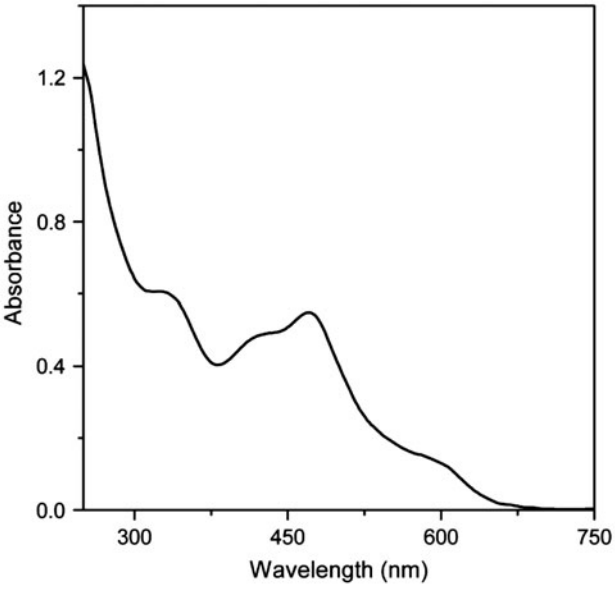


Figure 3. Electronic absorption spectrum of $[Co\{Co(abt)_3\}_2](ClO_4)_3 \cdot 2CH_3CN$ in methanol.

complex at ca. 470, 434, and 324 nm are much more intense than the d–d band; these bands are attributable to S→Co(III) charge transfer transitions among the bridging sulfur and central terminal cobalt ions.

## 4. Concluding remarks

We have synthesized and characterized an S-bridged tricobalt species bearing the aromatic aminobenzenethiolate by the direct treatment of $Co(ClO_4)_2$ with 2-aminobenzenethiol in air. The crystal structure of the meso form of the complex has been determined by X-ray crystallography, showing three thiolato-S donors of each terminal *fac*-(S)-$[Co(abt)_3]$ coordinating to the central Co to form a linear S-bridged tricobalt structure, $[Co\{Co(abt)_3\}_2]^{3+}$. Structurally, **1** is quite similar to other trinuclear metal complexes with aliphatic aminothiolates such as 2-aminoethanethiolate and L-cysteinate [25, 27, 29], except for the disposition of the ligand back bone with respect to the Co–Co–Co vector. Complex **1** represents the first-reported member of this class with the aromatic 2-aminobenzenethiolate.

## Supplementary material

CCDC 868772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: +44(0)1223-336033.

## Acknowledgments

A.P. acknowledges support from the University Grants Commission, India (Sanction No. PSW-173/11-12). D.M.E. acknowledges support from the National Center for Research Resources – NIH COBRE Award P20 RR017708.

## References

[1] B. Krebs, G. Henkel. *Angew. Chem. Int. Ed. Engl.*, **30**, 769 (1991).
[2] A. Sigel, H. Sigel, R.K.O. Sigel. *Metal Ions in Life Sciences*, Vol. 2: Nickel and Its Surprising Impact in Nature, Wiley, Chichester (2007).
[3] J.R. Zimmerman, B.W. Smucker, R.P. Dain, M.J. Van Stipdonk, D.M. Eichhorn. *Inorg. Chim. Acta*, **373**, 54 (2011).
[4] A. Panja, D.M. Eichhorn. *Inorg. Chim. Acta*, **391**, 88 (2012).
[5] A. Panja, D.M. Eichhorn. *J. Coord. Chem.*, **62**, 2600 (2009).
[6] B.W. Smucker, M.J. Van Stipdonk, D.M. Eichhorn. *J. Inorg. Biochem.*, **101**, 1537 (2007).
[7] A. Panja, C. Campana, C. Leavitt, M.J. Van Stipdonk, D.M. Eichhorn. *Inorg. Chim. Acta*, **362**, 1348 (2009).
[8] M. Schubert. *J. Am. Chem. Soc.*, **53**, 3851 (1931).
[9] W. Hieber, R. Brück. *Z. Anorg. Allg. Chem.*, **269**, 13 (1952).
[10] R.G. Neville, G. Gorin. *J. Am. Chem. Soc.*, **78**, 4893 (1956).
[11] D.H. Busch, D.C. Jicha. *Inorg. Chem.*, **1**, 884 (1962).
[12] G.R. Brubaker, B.E. Douglas. *Inorg. Chem.*, **6**, 1562 (1966).
[13] A. Igashira-Kamiyama, T. Konno. *Acta Crystallogr., Sect. E*, **64**, m1519 (2008).
[14] N. Mahboob, Y. Miyashita, Y. Yamada, K. Fujisawa, K. Okamoto. *Inorg. Chim. Acta*, **357**, 75 (2004).
[15] K.I. Okamoto, S.I. Aizawa, T. Konno, H. Einaga, J. Hidaka. *Bull. Chem. Soc. Jpn.*, **59**, 3859 (1986).
[16] Y. Miyashita, N. Sakagami, Y. Yamada, T. Konno, J. Hidaka, K. Okamota. *Bull. Chem. Soc. Jpn.*, **71**, 661 (1998).

[17] T. Konno, K. Okamoto, J. Hidaka. *Acta Crystallogr., Sect. C*, **49**, 222 (1993).

[18] N. Amir, Y. Miyashita, M. Fujita, K. Fujisawa, K. Okamoto. *Mol. Cryst. Liq. Cryst.*, **428**, 101 (2005).

[19] N. Amir, M. Motonishi, M. Fujita, Y. Miyashita, K. Fujisawa, K. Okamoto. *Eur. J. Inorg. Chem.*, 1041 (2006).

[20] K. Okamoto, M. Matsumoto, Y. Miyashita, N. Sakagami, J. Hidaka, T. Konno. *Inorg. Chim. Acta*, **260**, 17 (1997).

[21] N. Mahboob, Y. Miyashita, Y. Yamada, K. Fujisawa, K. Okamoto. *Polyhedron*, **21**, 1809 (2002).

[22] T. Konno, K. Nakamura, K. Okamoto, J. Hidaka. *Bull. Chem. Soc. Jpn.*, **66**, 2582 (1993).

[23] Y. Miyashita, Y. Yamada, K. Fujisawa, T. Konno, K. Kanamori, K.I. Okamoto. *J. Chem. Soc., Dalton Trans*., 981 (2000).

[24] Y. Miyashita, M. Hamajima, Y. Yamada, K. Fujisawa, K. Okamoto. *J. Chem. Soc., Dalton Trans*., 2089 (2001).

[25] M.J. Heeg, E.L. Blinn, E. Deutsch. *Inorg. Chem.*, **24**, 1118 (1985).

[26] R.E. Marsh, M.J. Heeg, E. Deutsch. *Inorg. Chem.*, **25**, 118 (1986).

[27] H.Q. Yuan, A. Igashira-Kamiyama, K. Tsuge, T. Konno. *Chem. Lett.*, **38**, 704 (2009).

[28] H.Q. Yuan, A. Igashira-Kamiyama, T. Konno. *Chem. Lett.*, **40**, 285 (2011).

[29] H.Q. Yuan, A. Igashira-Kamiyama, T. Konno. *Chem. Lett.*, **39**, 1212 (2010).

[30] *SAINT Software Reference Manual* (Version 4), Bruker AXS Inc., Madison, WI, USA.

[31] G.M. Sheldrick. *Acta Cryst. (A)*, **64**, 112 (2008).

[32] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Cryst.*, **42**, 339 (2009).