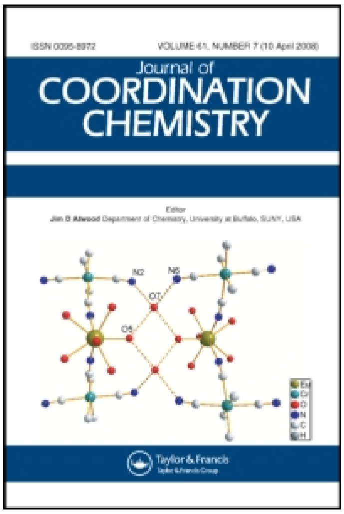


**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Chiral heterocyclic ligands. XVII. Pyridine-amino acid hybrid ligands: synthesis and crystal structures of metal complexes of a chelating ligand derived from L-alanine

William Lewis[a]; Peter J. Steel[a]
[a] Department of Chemistry, College of Science, University of Canterbury, Christchurch, New Zealand

First published on: 04 January 2011

**To cite this Article** Lewis, William and Steel, Peter J.(2011) 'Chiral heterocyclic ligands. XVII. Pyridine-amino acid hybrid ligands: synthesis and crystal structures of metal complexes of a chelating ligand derived from L-alanine', Journal of Coordination Chemistry, 64: 1, 115 — 121, First published on: 04 January 2011 (iFirst)

**To link to this Article: DOI:** 10.1080/00958972.2010.544302

**URL:** http://dx.doi.org/10.1080/00958972.2010.544302

*Journal of Coordination Chemistry*
Vol. 64, No. 1, 10 January 2011, 115–121

# Chiral heterocyclic ligands. XVII. Pyridine–amino acid hybrid ligands: synthesis and crystal structures of metal complexes of a chelating ligand derived from L-alanine

WILLIAM LEWIS and PETER J. STEEL*

Department of Chemistry, College of Science, University of Canterbury,
Christchurch, New Zealand

(*Received 19 August 2010; in final form 6 October 2010*)

A hybrid L-alanine–picolinamide is shown to act as an N,O-chelating ligand upon reaction with copper(II) nitrate and silver(I) perchlorate. X-ray crystal structures reveal that both these chiral complexes further assemble into 1-D polymeric chains through hydrogen bonding associations.

*Keywords*: Copper; Silver; N Ligands; Chiral ligands

## 1. Introduction

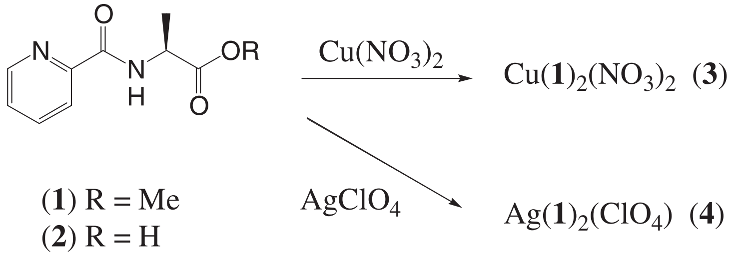
For many years, we have been involved in the synthesis of chiral heterocyclic ligands for use as chiral auxiliaries and as components in the construction of chiral metallosupramolecular assemblies [1, 2]. In this context, we have prepared a diverse range of ligands from the readily available monoterpene camphor, to which we have fused pyrazole [3, 4], pyrimidine [5], and pyrazine [6–8] rings. We have also used the common alkaloid nicotine as a bridging ligand for the formation of chiral silver coordination polymers [9]. More recently, we have described the synthesis of a number of metal complexes of a biheterocyclic ligand derived from the natural amino acid L-cysteine [10]. We now report the extension of this ligand design concept to the syntheses and X-ray crystal structures of two metal complexes of a hybrid ligand composed of a pyridine donor unit linked to the chiral amino acid L-alanine.

The ligand (**1**) that is the focus of this study has previously been the subject of a single report that suggested it might offer an *N*,*N*-chelating bidentate binding domain to copper [11]. We now demonstrate, using X-ray crystallography, that it actually acts as an N,O-chelating ligand to both copper(II) and silver(I).

---

*Corresponding author. Email: peter.steel@canterbury.ac.nz

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.544302



Scheme 1. Syntheses of **3** and **4**.

## 2. Experimental

### 2.1. *General experimental*

Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. The Campbell microanalytical laboratory at the University of Otago performed elemental analyses. NMR spectra were recorded on a Varian 500 MHz spectrometer at 23°C using a 3-mm probe. (*S*)-N-(Picolinamide)alanine methyl ester (**1**) was prepared by a modification of a reported procedure [11]. The $^{1}$H- and $^{13}$C-NMR spectra were in excellent agreement with literature values [12]. Lithium hydroxide induced hydrolysis of ester **1** produced the free acid **2** as colorless plates in quantitative yield [13].

### 2.2. *Preparation of the complexes*

**2.2.1. Cu(1)$_2$(NO$_3$)$_2$ (3).** A solution of (*S*)-N-(picolinamide)alanine methyl ester (21 mg, 0.1 mmol) in acetonitrile (1 mL) was added to a solution of copper(II) nitrate trihydrate (12 mg, 0.05 mmol) dissolved in acetonitrile (2 mL). The solution darkened immediately. Slow diffusion of diethyl ether into this solution provided pale blue plates suitable for X-ray diffraction. Yield 20 mg (80%), m.p. 164–166°C (dec.). Anal. Found: C, 39.81; H, 4.08; and N, 13.75. Calcd for $C_{20}H_{24}CuN_6O_{12}$: C, 39.77; H, 4.01; and N, 13.91. IR (KBr mull): 3163, 2231, 1695, 1510, 1076, 977, 957, 870, 802, and 733 cm$^{-1}$ (scheme 1).

**2.2.2. Ag(1)$_2$(ClO$_4$) (4).** A solution of (*S*)-N-(picolinamide)alanine methyl ester (21 mg, 0.1 mmol) in acetonitrile (1 mL) was added to a solution of silver(I) perchlorate (11 mg, 0.05 mmol) dissolved in acetonitrile (2 mL). The solution was kept in the dark. Slow diffusion of ethyl acetate into this solution, followed by almost complete evaporation of the solvent, resulted in colorless blocks suitable for X-ray crystallography. Yield *ca.* 8 mg. This complex was unstable upon removal from the mother liquor (scheme 1).

### 2.3. *X-ray crystallography*

Crystal data, data collection, and refinement parameters for all three structures are given in table 1. The measurements were made with a Siemens SMART CCD area detector for **2** and **3** and an APEX II area detector for **4** using graphite monochromated

Table 1. Crystal data and X-ray experimental data for **2**–**4**.

| Compound | **2** | **3** | **4** |
|---|---|---|---|
| Empirical formula | $C_9H_{10}N_2O_3$ | $C_{20}H_{24}CuN_6O_{12}$ | $C_{20}H_{24}AgClN_4O_{10}$ |
| Formula weight | 194.19 | 603.99 | 623.75 |
| Temperature (K) | 93(2) | 93(2) | 93(2) |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_1$ | $P2_12_12_1$ |
| Unit cell dimensions (Å, °) | | | |
| $a$ | 4.924(1) | 7.3304(3) | 8.3738(2) |
| $b$ | 10.107(2) | 13.7677(8) | 14.8936(4) |
| $c$ | 18.813(4) | 12.2355(7) | 19.9557(6) |
| $\beta$ | 90 | 92.301(2) | 90 |
| Volume (Å$^3$), $Z$ | 936.2(3), 4 | 1233.8(1), 2 | 2488.8(1), 4 |
| Calculated density (Mg m$^{-3}$) | 1.378 | 1.626 | 1.665 |
| Absorption coefficient (mm$^{-1}$) | 0.105 | 0.962 | 0.978 |
| $T_{min}/T_{max}$ | 0.861/1.000 | 0.812/1.000 | 0.878/1.000 |
| $F(0\,0\,0)$ | 408 | 622 | 1264 |
| Crystal size (mm$^3$) | 0.41 × 0.40 × 0.09 | 0.48 × 0.18 × 0.01 | 0.40 × 0.23 × 0.17 |
| $\theta$ range for data collection (°) | 2.17–26.43 | 1.67–30.71 | 2.46–26.35 |
| Reflections collected | 19,635 | 21,558 | 28,515 |
| Independent reflections | 1155 [$R$(int) = 0.0246] | 6454 [$R$(int) = 0.0470] | 5067 [$R$(int) = 0.0293] |
| Observed reflections (for $I > 2\sigma(I)$) | 1115 | 4936 | 4935 |
| Data/restraints/parameters | 1155/0/128 | 6454/1/365 | 5067/0/329 |
| Goodness-of-fit on $F^2$ | 1.061 | 1.011 | 1.045 |
| $R_1$ (for $I > 2\sigma(I)$) | 0.0249 | 0.0426 | 0.0167 |
| $wR_2$ (all data) | 0.0671 | 0.0889 | 0.0418 |

Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation. The intensities were corrected for Lorentz and polarization effects and for absorption [14]. The structures were solved by direct methods using SHELXS [15] and refined on $F^2$ using all data by full-matrix least-squares procedures using SHELXL [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens were included in calculated positions with isotropic displacement parameters 1.2 (aromatic) or 1.5 (aliphatic) times the isotropic equivalent of their carrier carbons.

## 3. Results and discussion

(*S*)-N-(Picolinamide)alanine methyl ester (**1**) has a number of potential coordination modes. Before preparing metal complexes of **1**, we decided it would be of interest to confirm the structure and conformation of the free ligand itself. However, since ligand **1** is not crystalline, we decided to hydrolyze the ester moiety to the corresponding acid (**2**). This provided a crystalline compound whose structure was determined by X-ray crystallography.

Acid **2** crystallizes in the orthorhombic space group $P2_12_12_1$, with one molecule in the asymmetric unit. There is an intramolecular interaction (2.24(1) Å) between the pyridine nitrogen (N6) and the amide hydrogen (H3A) which holds the pyridine ring coplanar with the adjacent amide group (figure 1). A search of the Cambridge Crystallographic Database [17] located 27 organic picolinamide derivatives [18], all of which had a similar relative orientation of these two groups and a similar intramolecular hydrogen bond.

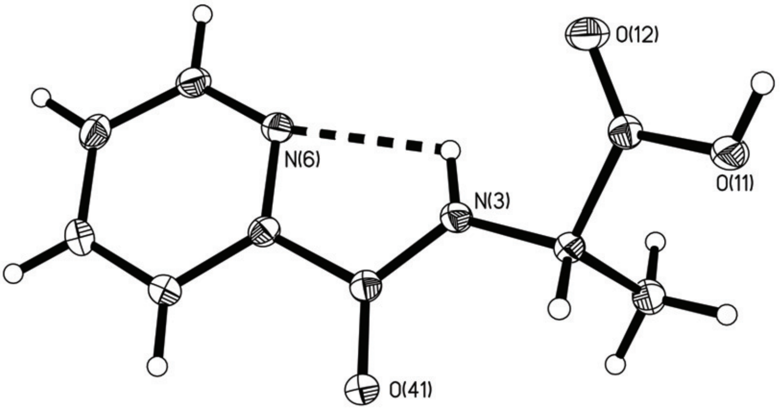


Figure 1. A perspective view of the X-ray structure of **2**. The intramolecular hydrogen bond between the pyridine nitrogen and amide is shown as a dashed line. Hydrogens are shown as spheres of arbitrary radius.

The extended structure of **2** features a 1-D hydrogen-bonded polymer that propagates along the *y*-axis. The polymer can be viewed as the polar core where the hydrogen bonding occurs, with the non-polar parts of the molecules forming the outside. The difference in size between the methyl and pyridine groups creates pockets, into which the pyridine rings of the adjacent polymer chains interdigitate in the *z*-direction. The pyridine rings have edge-to-face $\pi$-stacking interactions between adjacent rings (figure 2).

Reaction of two equivalents of **1** with one equivalent of copper nitrate in acetonitrile furnished a crystalline product (**3**) in good yield. It crystallizes in the monoclinic space group $P2_1$ as a 2 : 1 ligand : metal complex. The asymmetric unit contains the metal center coordinated to two molecules of **1** and two nitrates (figure 3). Both ligands chelate the copper center through the pyridine nitrogen and the amide oxygen, with bite angles of 82.57(11)° and 82.82(11)°. The two chelating ligands are coordinated in the same plane, with the nitrates occupying the axial positions. The Cu–O bonds to the nitrate anions are Jahn–Teller distorted, as is expected in such complexes: 2.405(3) and 2.425(3) Å compared to the 1.970(3)–1.991(2) Å for the equatorial ligands. The bonding geometry at the copper center is similar to that in related complexes of picolinamides with similar donor sets [19–23]. Any potential crystallographic center of inversion is forbidden by the chiral nature of the ligand, and the fact that appended arms of the two ligands have different conformations. Each complex participates in four hydrogen bonds between amide hydrogens and nitrate oxygens of adjacent complexes, which assembles the molecules into a 1-D chain that propagates in the *x*-direction (figure 4).

Reaction of two equivalents of **1** with one equivalent of silver perchlorate in acetonitrile furnished a few crystals of **4** in low yield. It crystallizes in the orthorhombic space group $P2_12_12_1$ as a 2 : 1 ligand : metal complex. The asymmetric unit consists of the metal center chelated by the pyridine nitrogen and amide oxygen of both ligands, and is completed by a perchlorate counter ion, which is hydrogen bonded to the complex (figure 5). The geometry of the silver center is distorted tetrahedral, with the bite angles of the chelate rings being 71.15(5)° and 71.44(5)°, while the other angles around the silver range from 105.73(4)° to 151.11(5)°. This wide range is due to the constrained geometry of the chelate ring, which in turn causes the other angles to widen. In this complex, the bonds to the pyridine nitrogens are shorter than those to the

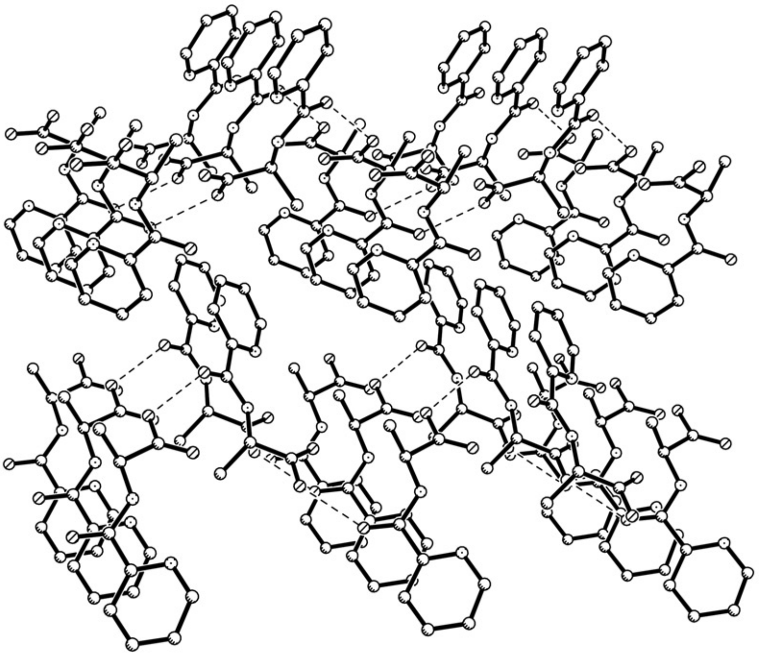


Figure 2. A packing diagram showing the $\pi$-stacking and hydrogen bonding between molecules of **2**.

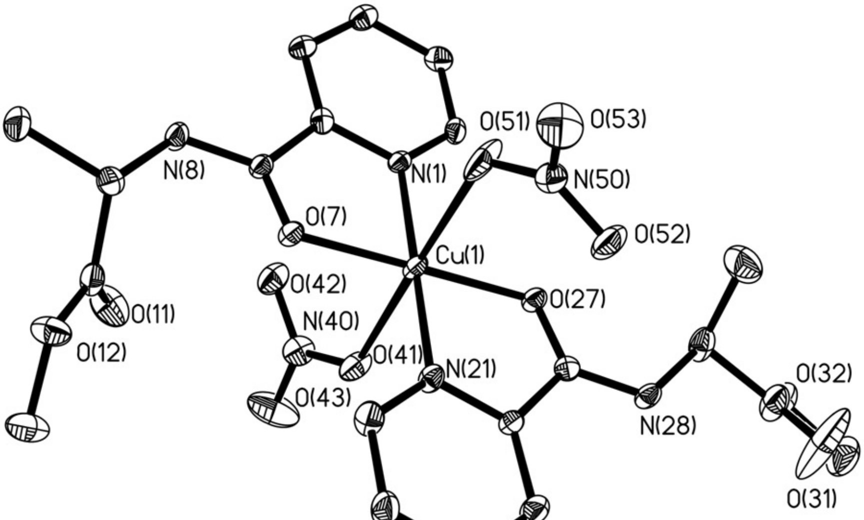


Figure 3. A perspective view of **3**. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.970(3), Cu(1)–O(7) 1.991(2), Cu(1)–N(21) 1.970(3), Cu(1)–O(27) 1.988(2), Cu(1)–O(41) 2.405(3), Cu(1)–O(51) 2.425(3), N(1)–Cu(1)–O(7) 82.57(11), N(1)–Cu(1)–N(21) 179.01(14), N(1)–Cu(1)–O(27) 97.88(11), N(1)–Cu(1)–O(41) 96.77(10), N(1)–Cu(1)–O(51) 84.61(12), O(7)–Cu(1)–N(21) 96.73(11), O(7)–Cu(1)–O(27) 179.54(13), O(7)–Cu(1)–O(41) 91.25(9), O(7)–Cu(1)–O(51) 89.06(10), N(21)–Cu(1)–O(27) 82.82(11), N(21)–Cu(1)–O(41) 83.94(11), N(21)–Cu(1)–O(51) 94.68(12), O(27)–Cu(1)–O(41) 88.63(9), O(27)–Cu(1)–O(51) 91.05(10), and O(41)–Cu(1)–O(51) 178.61(12).

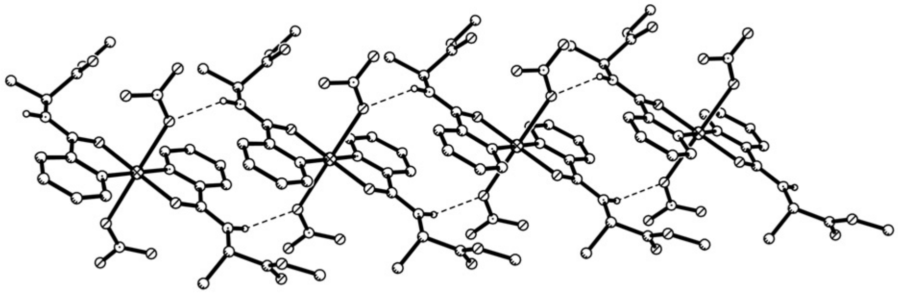


Figure 4. The 1-D hydrogen-bonded polymeric chain propagating along the *a*-axis.

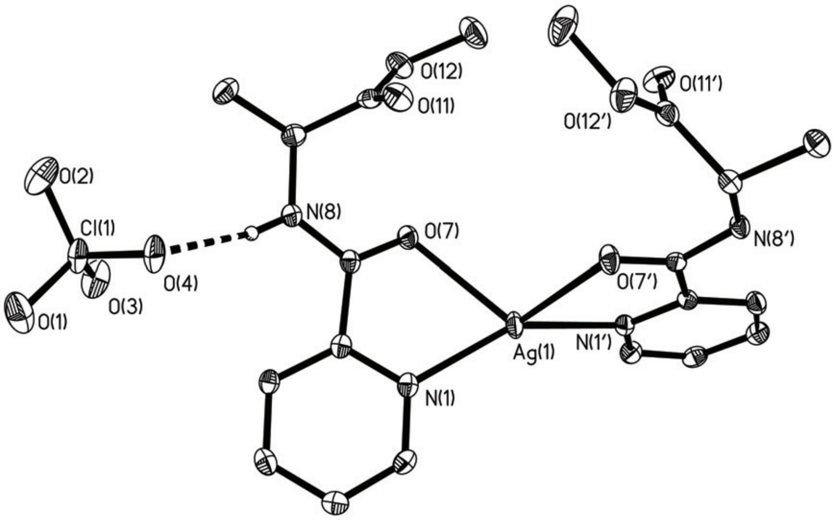


Figure 5. The asymmetric unit of **4**. The hydrogen bonding proton is represented by a sphere of arbitrary radius. Other hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.2280(15), Ag(1)–O(7) 2.4741(13), Ag(1)–N(1′) 2.2147(15), Ag(1)–O(7′) 2.4520(12), N(1)–Ag(1)–O(7′) 71.44(5), N(1)–Ag(1)–N(1′) 151.11(5), N(1)–Ag(1)–O(7′) 125.32(5), O(7)–Ag(1)–N(1′) 131.13(5), O(7)–Ag(1)–O(7′) 105.73(4), and N(1′)–Ag(1)–O(7′) 71.15(5).

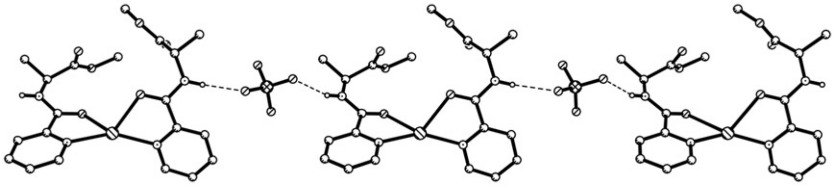


Figure 6. The 1-D hydrogen-bonded chain propagating along the *b*-axis.

amide oxygens. Double hydrogen bonding of the perchlorate anion again leads to a 1-D hydrogen-bonded chain (figure 6) that propagates along the *b*-axis.

In conclusion, we have shown that chiral ligand **1** acts as an N,O chelating ligand with both copper(II) and silver(I), rather than as the *N*,*N*-chelate previously suggested.

A search of the Cambridge Crystallographic Database [17] suggests that **4** is the first structure of a silver complex of a chelating picolinamide derivative.

## Supplementary material

Crystallographic data for **2–4** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 789505 – 789507). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

## References

[1] P.J. Steel. *Acta Crystallogr.*, **C39**, 1623 (1983).
[2] P.J. Steel. *Acc. Chem. Res.*, **38**, 243 (2005).
[3] A.A. Watson, D.A. House, P.J. Steel. *J. Organomet. Chem.*, **311**, 387 (1986).
[4] A.A. Watson, D.A. House, P.J. Steel. *J. Org. Chem.*, **56**, 4072 (1991).
[5] A.J. Downard, P.J. Steel, J. Steenwijk. *Aust. J. Chem.*, **48**, 1625 (1995).
[6] C.M. Fitchett, P.J. Steel. *New J. Chem.*, **24**, 945 (2000).
[7] C.M. Fitchett, P.J. Steel. *Aust. J. Chem.*, **59**, 19 (2006).
[8] C.M. Fitchett, P.J. Steel. *Dalton Trans.*, 4886 (2006).
[9] W. Lewis, P.J. Steel. *Supramol. Chem.*, **17**, 579 (2005).
[10] W. Lewis, P.J. Steel. *Tetrahedron*, **29**, 2220 (2010).
[11] K. Yamada, H. Ozaki, N. Okumura, O. Mabuchi, H. Yamamura, S. Araki, R. Katakai, M. Kawai. *Peptide Chem.*, **34**, 485 (1996).
[12] A. Takacs, B. Jakab, A. Petz, L. Kollar. *Tetrahedron*, **63**, 10372 (2007).
[13] K.V. Reddy, S.-J. Jin, P.K. Arora, D.S. Sfeir, S.C.F. Maloney, F.L. Urbach, L.M. Sayre. *J. Am. Chem. Soc.*, **112**, 2332 (1990).
[14] R.H. Blessing. *Acta Crystallogr.*, **A51**, 33 (1995).
[15] G.M. Sheldrick. *Acta Crystallogr.*, **A46**, 467 (1990).
[16] G.M. Sheldrick. *Acta Crystallogr.*, **A64**, 112 (2008).
[17] F.H. Allen, R. Taylor. *Chem. Soc. Rev.*, **33**, 463 (2004).
[18] See for example: (a) F.S. Stephens, R.S. Vagg. *Inorg. Chim. Acta*, **142**, 43 (1988); (b) T. Moriuchi, M. Nishiyama, K. Yoshida, T. Ishikawa, T. Hirao. *Org. Lett.*, **3**, 1459 (2001); (c) J.Y. Qi, Q.Y. Yang, K.H. Lam, Z.Y. Zhou, A.S.C. Chan. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **59**, o374 (2003); (d) S.-M. Shi, B. Jia, Y. Wu, X.-D. Liu, Z.-Q. Hu. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **62**, o2278 (2006); (e) Q. Zhang, S.-P. Zhang, S.-C. Shao. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **62**, o4695 (2006); (f) S. Meghdadi, H.R. Khavasi, S. Nalchigar. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **62**, o5492 (2006); (g) A. Behrens, D. Rehder. *Inorg. Chem. Commun.*, **9**, 708 (2006); (h) G. Gasser, H. Stoeckli-Evans. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **63**, o1455 (2007); (i) S.-C. Chen, F.-H. Yin, M.-Y. He, K. Yan, Q. Chen. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **63**, o2835 (2007); (j) S.-J. Gu, J. Lin, L.-H. Jing, H.-X. Zhang, D.-B. Qin. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **63**, o3205 (2007); (k) J.-F. Zheng, S.-Y. Huang, J.-N. Guo, Y. Zhang, L.-R. Jin. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **64**, o1362 (2008); (l) Y.-G. Zhuang, H.-J. Jiang, Z. Hong, F.-L. Qiu. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **64**, o1904 (2008); (m) P. Srinivas, P.R. Likhar, H. Maheshwaran, B. Sridhar, K. Ravikumar, M.L. Kantam. *Chem. Eur. J.*, **15**, 1578 (2009).
[19] A. Morsali, A. Ramazani, A.R. Mahjoub. *J. Coord. Chem.*, **56**, 1555 (2003).
[20] L. Sieron, M. Bukowska-Strzyzewska. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **53**, 296 (1997).
[21] H. Ruan, H.-W. Chen, R.-C. Xuan. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **63**, m1855 (2007).
[22] I. Ucar, A. Bulut, O.Z. Yesilel, H. Olmez, O. Buyukgungor. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **60**, m1945 (2004).
[23] L. Sieron. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **63**, m862 (2007).