

# Maleate–fumarate conversion and other novel aspects of the reaction of a Co(II) maleate with pyridine and bipyridine†

M. Padmanabhan,<sup>a</sup> James C. Joseph,<sup>a</sup> A. Thirumurugan<sup>b</sup> and C. N. R. Rao<sup>\*b</sup>

Received 3rd December 2007, Accepted 25th February 2008

First published as an Advance Article on the web 26th March 2008

DOI: 10.1039/b718623a

Reaction of a molecular Co(II) maleate,  $[\text{Co}(\text{Hmal})_2(\text{H}_2\text{O})_4]$ , with pyridine yields a Co(II) fumarate,  $[\text{Co}(\text{fum})(\text{H}_2\text{O})_4]$ , with a chain structure and a chiral pyridylsuccinic acid zwitter ion,  $^-\text{OOC}-\text{CH}(\text{N}^+\text{C}_5\text{H}_5)-\text{CH}_2-\text{COOH}$ , in almost quantitative yields, while the reaction of 4,4'-bipyridine (bipy) with the Co(II) maleate, on the other hand, almost quantitatively generates a polymeric Co(II) maleate,  $[\text{Co}(\text{mal})(\text{bipy})]_n \cdot (n/2)\text{H}_2\text{O}$  along with the adduct of fumaric acid with bipyridine.

Isomeric maleic and fumaric acids have been used as bridging ligands in generating metal–organic coordination polymers with diverse and interesting structural features.<sup>1–2</sup> Several metal derivatives of these dicarboxylic acids possessing interesting structures with or without any auxiliary ligands have been described in the literature.<sup>3–17</sup> In the absence of other strongly coordinating multidentate ligands, metal(II) fumarates tend to form linear or zig-zag polymeric chain structures with the *trans* carboxylate functions acting as the bridging units.<sup>1</sup> Metal(II) maleates do not form such one-dimensional structures because of the sterically crowded disposition of the carboxyl groups. While working with metal maleates (mal) and fumarates (fum), we have encountered two types of cobalt(II) maleates,  $[\text{Co}(\text{mal})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ , **1**, and  $[\text{Co}(\text{Hmal})_2(\text{H}_2\text{O})_4]$ , **2** whose structures are known.<sup>16</sup> The violet-coloured compound **1** containing the dianionic maleate ion ( $\text{mal}^{2-}$ ) with a metal : maleate ratio of 1 : 1, has a three-dimensional structure, with the carboxylate moiety acting as the bridging unit between Co(II) ions. **2** is a molecular compound with the maleate in the mono-deprotonated form ( $\text{malH}^{1-}$ ) and a metal : maleate ratio of 1 : 2 (Fig. 1). Molecular compounds and coordination polymers based on **1** involving Lewis bases are known.<sup>18</sup> Thus, with pyridine **1** forms a simple adduct. However, there are no reports on the reaction of **2** with pyridine or other Lewis bases. We have found an unexpected transformation wherein **2**, on reaction with pyridine, yields a linear chain cobalt(II) fumarate along with a chiral pyridylsuccinic acid zwitter ion. On carrying out the reaction of **2** with 4,4'-bipyridine (bipy), we do not observe the formation of a chiral zwitter ion analogue or the transformation of the cobalt(II) maleate to the cobalt fumarate. Instead, we obtain the adduct of fumaric acid with bipyridine and a polymeric cobalt(II) maleate. We describe these unusual transformations in this communication.

<sup>a</sup>School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills, Kottayam, 686 560, Kerala, India

<sup>b</sup>Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore, 560064, India. E-mail: cnrao@jncasr.ac.in; Fax: +91 (0)80 2208 2766

† CCDC reference numbers 611831 & 611832. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718623a Electronic supplementary information (ESI) available: Thermogravimetric analysis of **5**. See DOI: 10.1039/b718623a

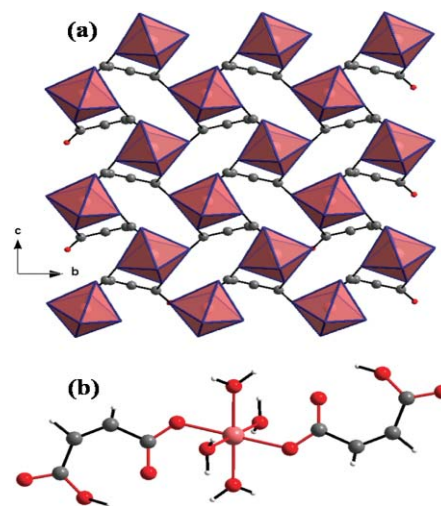
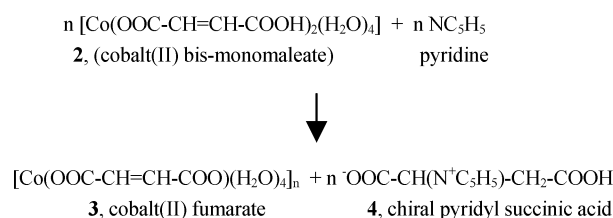


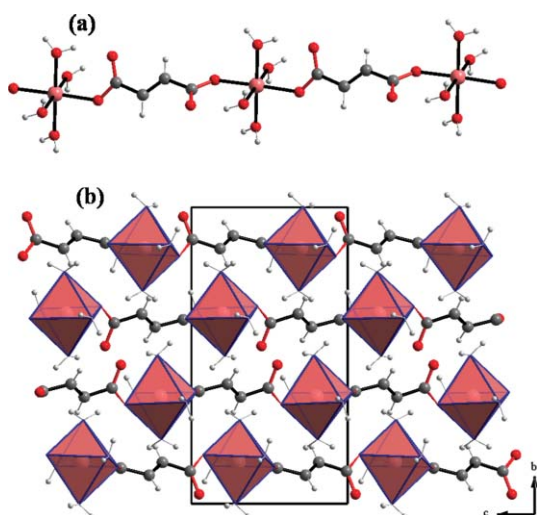
Fig. 1 The extended 3-dimensional structure of **1** (a) and that of the molecular compound **2** (b).

Reaction of **2** with pyridine yields a pink coloured cobalt(II) compound **3** and a colourless organic compound **4** in nearly quantitative yields.‡



**3**, with the composition  $[\text{Co}(\text{C}_4\text{H}_2\text{O}_4)(\text{H}_2\text{O})_4]_n$ , has an asymmetric unit containing 13 non-hydrogen atoms. The structure of **3** comprises a one-dimensional chain formed by fumarate units (Fig. 2).§†

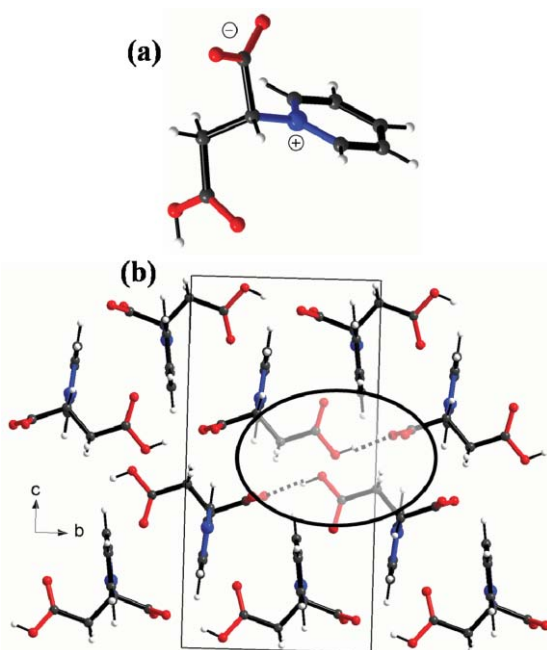
Clearly, the maleate in **2** transforms completely to the fumarate on reaction with pyridine. The Co(II) ion in **3** is coordinated by four different water molecules which form a plane of a distorted  $\text{CoO}_6$  octahedron. The remaining two oxygens situated in the opposite corners of the octahedron are from two monodentate fumarate units. The fumarate units link the two  $\text{CoO}_6$  octahedral units giving rise to the infinite one-dimensional structure. The structure of **3** is stabilized by both *intra*- and *inter*-chain hydrogen bonding interactions among the coordinated water molecules or between the water and the carboxylate ions. The Co–O bond distances in **3** are in the range 2.084(2)–2.133(2) Å. The other product we could isolate from the reaction of pyridine with **2** was a



**Fig. 2** The molecular structure of **3** showing linear 1-D arrangement (a) and packing features (b).

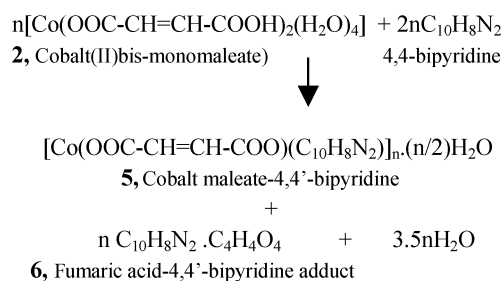
colorless, water-soluble crystalline organic compound **4**, analyzing for the composition  $C_9H_9NO_4$ .<sup>¶</sup>

**4** is not a pyridinium salt of maleate or fumarate but a zwitter ion where the pyridine bonds to an olefinic carbon of maleic acid (Fig. 3) as reported earlier.<sup>19</sup> **4** contains both carboxylate ion and carboxylic acid functions. Besides being a zwitter ion with a positive charge on the pyridinium nitrogen and a negative charge on the carboxylate, group, it is chiral and occurs as racemic mixture. The structure of **4** is stabilised by strong intermolecular H-bonds between the free COOH group and the negatively charged carboxylate oxygen. The  $O \cdots O$  and  $H \cdots O$  distances are 2.5393(19) and 1.731(2) Å, respectively, and the  $O-H \cdots O$  angle is 168.3(2)°.



**Fig. 3** Molecular structure (a) and packing diagram (b) of **4**, where the hydrogen bonding pattern is highlighted.

Motivated by the above transformation of **2** on reaction with pyridine, we thought of generating a dichiral product by reacting 4,4'-bipyridine (bipy) with **2** under similar conditions. Surprisingly, no chiral product of the type **4** was obtained. Out of the two products (**5**, **6**) of this reaction\*<sup>†</sup>, the metal-containing compound was analyzed for  $[Co(C_4H_2O_4)(C_{10}H_8N_2)] \cdot 0.5H_2O$ , **5**, and found to contain bipy along with a coordinated maleate and not a fumarate moiety. The identity of **5** as a maleate was confirmed by chemical analysis, FTIR and UV-visible spectra and powder X-ray diffraction (PXRD) data. The structure of **5** appears to be similar to that of the manganese compound reported by Shi *et al.*<sup>6</sup> **6** is the 1 : 1 adduct formed between 4,4'-bipyridine and fumaric acid.<sup>20</sup> The authenticity of **6** was confirmed by chemical analysis, FTIR, <sup>1</sup>HNMR and PXRD.



We had first carried out the above reaction by treating one equivalent of **2** with 0.5 equivalent of bipy anticipating the formation of the bi-zwitter ion and cobalt(II) fumarate, **3**. We obtained **5** and **6** along with a major quantity (about 0.75 equivalent) of unreacted **2**. On reacting **2** with twice its equivalent of bipy the conversion of **2** was complete to yield **5** and **6** quantitatively.

In conclusion, we feel that the quantitative formation of the chiral pyridyl succinic acid and the cobalt fumarate with a chain structure by the reaction of pyridine with the cobalt(II) bis-maleate **2** is unusual in terms of the maleate to fumarate transformation and also because of the formation of the chiral zwitter ion. Such *cis-trans* transformation is not altogether common.<sup>20</sup> The formation of the chiral zwitter ion may be of significance owing to the relevance of pyridinium zwitter ions in organic synthesis, biological transformations and preparation of novel materials.<sup>21</sup> The mechanism involved in the formation of chiral pyridinium zwitter ion **4** and also maleate to fumarate conversion by stoichiometric (1 : 1) reaction of pyridine on cobalt bis-maleate **2** would indeed be interesting and we feel that nucleophilic attack of the Lewis base (pyridine) on one of the electron deficient olefinic carbon atoms of the coordinated mono-maleate moiety could be crucial step involved in this.<sup>22</sup> We are currently looking at the interaction of several substituted pyridines with **2** and hope to get a better insight into this. Even though zwitter ions are generally reactive species, **4** is stable and can be recrystallised from hot aqueous solution. Attempts to resolve the racemic mixture to get optically pure components and employing them for synthesis of chiral derivatives are in progress. The reaction of **2** with bipy does not yield chiral zwitter ion product but gives rise to a bipy-fumaric acid adduct due to the *cis to trans* conversion of maleic acid to fumaric acid. Unlike in the reaction with pyridine, the metal-maleate does not transform to the metal-fumarate in this case.

## Notes and references

‡ **2** was prepared by reacting  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g, 1.0 mmol) with a solution of maleic acid (0.174 g, 1.5 mmol) in water and adjusting the pH to around 7.0 by the slow addition of dilute NaOH. When a clear solution so obtained was kept for 4 days reddish pink prismatic crystals of **2** were obtained in good yield. The powder diffraction pattern agreed with that generated from the known crystal structure.<sup>16</sup> After removing the crystals of **2**, the solution was further concentrated and kept for two more days when violet crystals of **1** were obtained in moderate yield. The sparingly soluble **1** when interacted with pyridine formed a pyridine adduct in solution but no solid product could be isolated. On the other hand, when we reacted **2** with pyridine in aqueous solution, two crystalline products **3** and **4** could be isolated in almost quantitative yields (92 and 94% respectively). Compound **4** initially separates out as colourless crystals, which are filtered out. The coloured solution obtained after removing **4** was evaporated to get a pink crystalline powder of **3** which was then recrystallised to get pink crystals of the compound.

§ Elemental analysis of **3** (%), calculated for  $\text{Co}(\text{C}_4\text{H}_{10}\text{O}_8)$  (245.05): C 19.59, H 4.1, found C 19.8, H 4.2. IR spectrum (KBr pellet) gave broad bands (in  $\text{cm}^{-1}$ ) in the region 3300–3500 ( $\nu(\text{O}-\text{H})$ , of  $\text{H}_2\text{O}$ ), 1558 vs ( $\nu_{\text{as}}, \text{O}-\text{C}=\text{O}$ ) and 1392 vs ( $\nu_s, \text{O}-\text{C}=\text{O}$ ). UV-visible spectrum:  $\nu_3 = 20100 \text{ cm}^{-1}$ ,  $\nu_2 = 15810 \text{ cm}^{-1}$  suggests Oh geometry. Thermogravimetry gave the first stage of mass loss in the range 125–180 °C which indicated the loss of four molecules of water. Crystallographic data for **3**,  $\text{Co}(\text{C}_4\text{H}_{10}\text{O}_8)$ .  $M = 245.05$ , monoclinic, space group  $P2(1)/c$  (no. 14),  $a = 7.5251(2)$ ,  $b = 14.4513(2)$ ,  $c = 7.7358(2)$  Å,  $\beta = 99.590(2)^\circ$ ,  $V = 829.49(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 293$  K,  $D(\text{calc}) = 1.962 \text{ g cm}^{-3}$ ,  $\mu = 2.084 \text{ mm}^{-1}$ . Intensity data were collected on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) operating at 40 kV and 40 mA. The structure was solved and refined using the SHELXTL-PLUS suite of programs.<sup>23</sup> There were 3369 measured reflections of which 1179 reflections ( $R_{\text{int}} = 0.0282$ ) were independent and all are included in the refinement.  $R_1 = 0.0246$ ,  $wR2 = 0.0643$  for 1087 observed reflections with  $[I > 2\sigma(I)]$ , and  $R1 = 0.0262$ ,  $wR2 = 0.0649$ , for all data.

¶ Elemental analysis of **4** (%), calculated for  $\text{C}_9\text{H}_9\text{NO}_4$  (195.17): C 55.3, H 4.61 and N 7.17, found C 54.9, H 4.7 and N 6.9. IR spectrum of **4**, showed in-plane and out-of-plane ring deformations of pyridine at 659 and 420  $\text{cm}^{-1}$  respectively besides a band at 1686  $\text{cm}^{-1}$  (free  $-\text{COOH}$ ) and  $\nu_{\text{as}}(\text{O}-\text{C}=\text{O})$  and  $\nu_s(\text{O}-\text{C}=\text{O})$  of the  $\text{COO}^-$  at 1577 and 1338  $\text{cm}^{-1}$ . UV-vis spectrum: sharp peak at 261 nm with a shoulder. <sup>1</sup>H NMR data of **4**:  $\delta_{\text{H}}$  (400 MHz,  $\text{D}_2\text{O}$ ) 3.22 (1H, dd,  $\text{CH}_2$ ), 3.35 (1H, dd,  $\text{CH}_2$ ), 5.47 (1H, dd, CH), 7.8 (2H, t, *meta*-H of pyridyl), 8.4 (1H, t, *para*-H of pyridyl), 8.73 (2H, d, *ortho*-H of pyridyl). The unusual downfield signals of the pyridine ring show the presence of the pyridinium zwitter ion.

\* An aqueous solution (10 mL) of **2** (1 mmol, 0.361 g) was refluxed with a methanolic solution (10 mL) of 4,4'-bipyridine (2 mmol, 0.312 g). A pink compound with a silky shining appearance was formed after a few seconds. The mixture was refluxed for 24 h and filtered. The precipitated pink compound **5** (yield 95%) was washed several times with water and dried. The filtrate obtained after separating out **5** yielded colourless, thin, needle shaped crystals of **6** after 2 days (yield 90%). Elemental analysis of **5** (%), calculated for  $\text{CoC}_{14}\text{H}_{11}\text{N}_2\text{O}_{4.5}$ : C, 49.71; H, 3.25; N, 8.28, found C, 49.04; H, 3.03; N, 8.19. IR (KBr disc;  $\text{cm}^{-1}$ ) 3425 [ $\nu(\text{O}-\text{H})$ ], 1558 [ $\nu_{\text{as}}(\text{O}-\text{C}=\text{O})$ ], 1416, 1392 [ $\nu_s(\text{O}-\text{C}=\text{O})$ ], 1614, 1431 and 1011 (coordinated bipy), 1045 [ $\nu(\text{CN})$ ]. TG analysis showed the presence of 0.5 equivalent of water of crystallisation in **5**. Elemental analysis of **6** (%), calculated for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 61.76; H, 4.41; N, 10.29, found: C, 62.22; H, 4.81; N, 10.22 IR (KBr disc,  $\text{cm}^{-1}$ ) 1701 (free  $\text{COOH}$ ), 1581 and 1407 [ $\nu_{\text{as}}(\text{O}-\text{C}=\text{O})$  and  $\nu_s(\text{O}-\text{C}=\text{O})$ ], 1601, 1431, 1010 (bipy) and 1040 [ $\nu(\text{CN})$ ]. <sup>1</sup>H NMR of compound **6**:  $\delta_{\text{H}}$  [300 MHz,  $\text{D}_2\text{O}$ , 300 K] 8.86 (d, 4H *ortho*, bipy), 8.18 (d, 4H *meta*, bipy), 6.68 (s, 2H fumaric acid), 8.8 (d, 4H *ortho*, bipy), 8.1 (d, 4H *meta*, bipy), 6.5 (4H fumaric acid).

1 (a) D. M. Young, U. Geiser, A. J. Schultz and H. H. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 1331; (b) K. Seki, S. Takamizawa and W. Mori, *Chem. Lett.*, 2001, 122; (c) S. Konar, E. Zangrando and N. R. Chaudhuri,

*Inorg. Chim. Acta*, 2003, **355**, 264; (d) Y. Zheng and H. Xie, *J. Solid State Chem.*, 2004, **177**, 1352.

- 2 (a) D. Ghoshal, G. Mostafa, T. K. Maji, E. Zangrando, T. Lu, J. Ribas and N. R. Chaudhuri, *New J. Chem.*, 2004, **28**, 1204; (b) N. P. Porollo, Z. G. Aliev, G. I. Dzhardimalieva, I. N. Ivleva, I. E. Uflyand, A. D. Pomogailo and N. S. Ovanesyan, *Russ. Chem. Bull.*, 1997, **46**, 362; (c) E. Pajtasova, E. Jona, M. Koman and D. Ondrusova, *Pol. J. Chem.*, 2001, **75**, 1209.
- 3 C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466.
- 4 N. Guillou, S. Pastre, C. Levage and G. Ferey, *Chem. Commun.*, 2002, 2358.
- 5 Y. Q. Zheng, Z. P. Kong and B. Y. Chen, *J. Chem. Crystallogr.*, 2002, **32**(10), 399.
- 6 Z. Shi, L. Zhang, S. Gao, G. Yang, J. Hua, L. Gao and S. Feng, *Inorg. Chem.*, 2000, **39**, 1990.
- 7 K. Seki and W. Mori, *J. Phys. Chem. B*, 2002, **106**, 1380.
- 8 E.-B. Ying, Y.-Q. Zheng and Q.-Q. Zhou, *Z. Kristallogr. NCS*, 2004, **219**, 65.
- 9 W. Mori, S. Takamizawa, C. N. Kato, T. Ohmura and T. Sato, *Microporous Mesoporous Mater.*, 2004, **73**, 31.
- 10 Y.-Q. Zheng, Z.-P. Kong and J.-L. Lin, *Z. Kristallogr. NCS*, 2002, **217**, 195.
- 11 (a) P. S. Mukherjee, T. K. Maji, G. Mostafa, J. Ribas, M. S. El. Fallah and N. R. Chaudhuri, *Inorg. Chem.*, 2001, **40**, 928; (b) P. S. Mukherjee, S. Konar, E. Zangrando, T. Mallah, J. Ribas and N. R. Chaudhuri, *Inorg. Chem.*, 2003, **42**, 2695; (c) P. S. Mukherjee, S. Dalai, G. Mostafa, E. Zangrando, T.-H. Lu, G. Rogz, T. Mallah and N. R. Chaudhuri, *Chem. Commun.*, 2001, 1346; (d) S. Dalai, P. S. Mukherjee, E. Zangrando, F. Lloret and N. R. Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 2002, 822; (e) S. Konar, P. S. Mukherjee, E. Zangrando, F. Lloret and N. R. Chaudhuri, *Angew. Chem., Int. Ed.*, 2002, **41**, 1561; (f) S. Konar, E. Zangrando, M. G. B. Drew, J. Ribas and N. R. Chaudhuri, *Dalton Trans.*, 2004, 260; (g) S. Sain, T. K. Maji, G. Mostafa, T. H. Lu and N. R. Chaudhuri, *New J. Chem.*, 2003, **27**, 185.
- 12 L. Huang and L.-P. Zhang, *THEOCHEM*, 2004, **692**, 249.
- 13 Y. Y. Wang, X. Wang and Q. Z. Shi, *Transition Met. Chem.*, 2002, **27**, 481.
- 14 A. D. Burrows, R. W. Harrington, M. F. Mahon and S. J. Teat, *Cryst. Growth Des.*, 2001, **4**, 813.
- 15 E. G. Bakalbassis, M. Korabik, A. Michailides, J. Mrozinski, C. Raptopoulou, S. Skoulika, A. Terzis and D. Tsaousis, *J. Chem. Soc., Dalton Trans.*, 2001, 850.
- 16 (a) M. P. Gupta and B. N. Saha, *Ind. Nat. Conf. Crystallogr.*, 1977, 13; (b) N. P. Porollo, Z. G. Aliev, G. I. Dzhardimalieva, I. N. Ivleva, I. E. Uflyand, A. D. Pomogailo and N. S. Ovanesyan, *Russ. Chem. Bull.*, 1997, 375.
- 17 M. Padmanabhan, S. Meena Kumari, X. Huang and Jing Li, *Inorg. Chim. Acta*, 2005, **358**, 3537.
- 18 (a) C. Zhang, D. Wu, K. Yu and D. Yan, *J. Coord. Chem.*, 2000, **51**, 93; (b) C. Yun, L. Ping, W. Jian, L. Qing-Yan and C. Wen-Dan, *Jieyou Huaxue*, 2004, **23**(3), 270.
- 19 M. N. G. James and M. Matsushima, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1976, **32**, 959.
- 20 S. Chatterjee, V. R. Pedireddi and C. N. R. Rao, *Tetrahedron Lett.*, 1998, **39**, 2843.
- 21 (a) B. S. Jursic, D. M. Neumann, Z. Moore and E. D. Stevens, *J. Org. Chem.*, 2002, **67**, 2372; (b) V. P. Litvinov, *Russ. J. Org. Chem.*, 1995, **31**, 1301; V. P. Litvinov, *Russ. J. Org. Chem.*, 1994, **30**, 1658; (c) K. V. Gothelf and K. A. Jorgensen, *Chem. Rev.*, 1998, **98**, 863; (d) T. A. Spencer, T. J. Onofrey, R. O. Cann, J. S. Russel, L. E. Lee, D. E. Blanchard, A. Castro, P. Gu, G. Jiang and I. Schechter, *J. Org. Chem.*, 1999, **64**, 807.
- 22 M. M. Kayser and O. Eisenstein, *Can. J. Chem.*, 1981, **59**, 2457.
- 23 (a) G. M. Sheldrick, *SADABS Siemens Area Detector Absorption Correction Program*, University of Göttingen, Göttingen, Germany, 1994; (b) G. M. Sheldrick, *SHELXTL-PLUS Program for Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen, Germany, 1997.