

Pyridinodithioacetate and its first stable metal complex †

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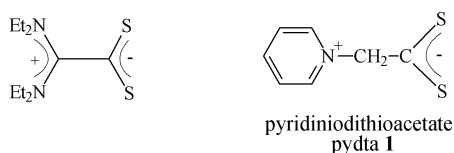
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The crystal structures of pyridinodithioacetate (pydta) **1** and its first stable metal complex, [Cd(pydta)₂Cl₂] **2**, have been determined; intermolecular C–H...S hydrogen bonds play a dominant role in determining the molecular packing of both structures, and **2** is further stabilized by the presence of weak C–H...Cl interactions.

Dithiocarboxylic acids and dithiocarbamic acids as ligands have been extensively studied due to their versatile coordination properties, their importance in probing the structure and function of active sites in some metalloenzymes, and their known pharmacological and fungicidal activities.¹ However, metal complexes of dithiocarboxylate betaines have been rarely studied, despite the fact that they exhibit significant anti-radiation and anti-cancer activities.² In our ongoing investigation on the coordination chemistry of carboxylate betaines and double betaines, it has been found that the naked carboxylate group of such zwitterionic ligands readily enters into the coordination sphere of the metal in a variety of binding modes.³ Our exploration is naturally extended to the coordination chemistry of dithiocarboxylate betaines.

The only known example of a well-characterized metal complex containing this type of neutral, dipolar ligand is Pt₂{μ-(Et₂N)₂C₂S₂}₂Cl₄·0.5CH₂Cl₂^{1b} ((Et₂N)₂C₂S₂ = bis(*N,N*-diethylamino)carbenium dithiocarboxylate) in which each dithiocarboxylate group bridges two Pt(II) atoms. However, (Et₂N)₂C₂S₂ is formally a carbenium derivative and therefore not a typical member of the dithiocarboxylate betaine family. Pyridinodithioacetate (pydta) **1**, a prototypal dithiocarboxylate betaine ligand, has been known since 1962,⁴ but detailed information on its structure and coordination properties is unavailable on account of its instability at room temperature. In the present report, we describe the isolation of its first stable metal complex [Cd(pydta)₂Cl₂] **2** and the crystal and molecular structures of both compounds. ‡



Dithiocarboxylate betaine **1** gradually turns black after storage for several days at room temperature, even in the solid state. It has low solubility in most solvents and is readily oxidized in basic or neutral solution. However, it is more stable in acidic solution and at low temperature. Attempts to prepare the Zn(II) and Hg(II) complexes with **1** in DMF were unsuccessful, as the ligand itself readily crystallized at low temperature. In addition, the reaction of **1** with a variety of salts of transition metals such as Cu(II), Cu(I), Ni(II) and Fe(II) resulted in a dark red solution which deposited a black sulfide precipitate after standing for one or two days at –15 °C.

The molecular structure, hydrogen-bonding pattern and atomic numbering scheme of **1** is depicted in Fig. 1, and selected

Table 1 Selected bond lengths (Å) and angles (°) for **1** and **2**

Compound 1			
S(1)–C(7)	1.679(3)	S(2)–C(7)	1.665(3)
C(7)–C(6)	1.527(4)	C(6)–N(1)	1.476(4)
S(1)–C(7)–S(2)	127.4(2)	C(6)–C(7)–S(1)	111.6(2)
C(6)–C(7)–S(2)	121.0(2)	N(1)–C(6)–C(7)	115.3(2)
Complex 2			
Cd(1)–Cl(1)	2.593(1)	Cd(1)–Cl(2)	2.469(2)
Cd(1)–S(1)	2.742(2)	Cd(1)–S(2)	2.707(1)
Cd(1)–S(3)	2.552(2)	S(1)–C(7)	1.657(4)
S(2)–C(7)	1.675(5)	S(3)–C(14)	1.699(4)
S(4)–C(14)	1.644(4)	N(1)–C(1)	1.338(6)
N(1)–C(6)	1.474(5)	N(2)–C(13)	1.482(5)
Cl(2)–Cd(1)–Cl(1)	102.60(4)	Cl(2)–Cd(1)–S(3)	117.29(6)
S(3)–Cd(1)–Cl(1)	83.77(4)	Cl(2)–Cd(1)–S(2)	102.58(5)
S(3)–Cd(1)–S(2)	105.41(4)	Cl(1)–Cd(1)–S(2)	145.10(5)
Cl(2)–Cd(1)–S(1)	102.48(6)	S(3)–Cd(1)–S(1)	140.19(6)
Cl(1)–Cd(1)–S(1)	86.26(5)	S(2)–Cd(1)–S(1)	64.94(4)
C(7)–S(1)–Cd(1)	85.7(2)	C(7)–S(2)–Cd(1)	86.5(2)
C(8)–S(3)–Cd(1)	111.5(2)	C(6)–C(7)–S(1)	115.9(3)
C(6)–C(7)–S(2)	121.3(3)	S(1)–C(7)–S(2)	122.8(3)
S(4)–C(14)–S(3)	127.2(3)	C(13)–C(14)–S(4)	121.3(3)
C(13)–C(14)–S(3)	111.4(3)	N(1)–C(6)–C(7)	113.4(4)
N(2)–C(13)–C(14)	113.3(3)		

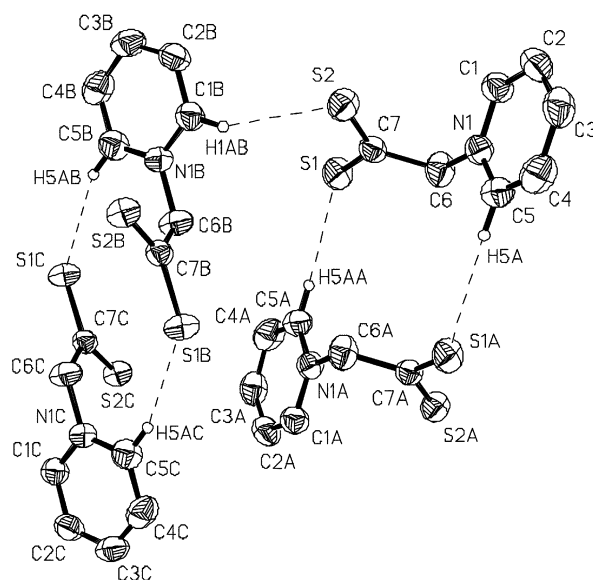


Fig. 1 Perspective view (thermal ellipsoids at the 35% probability level) of C₅H₅N⁺CH₂CS₂[–] (pydta) **1** with atomic numbering and hydrogen-bonding scheme. Hydrogen atoms other than those involved in hydrogen-bonding are omitted for clarity. Symmetry code: A 1 – x, –y, 1 – z; B x, ½ – y, –½ + z; C 1 – x, ½ + y, ½ – z.

bond lengths and bond angles are listed in Table 1. As anticipated, the dithiocarboxylate group lies almost perpendicular to the pyridyl ring (dihedral angle = 71.8°) and has essentially

† Dedicated to Prof. James Trotter on the occasion of his 70th birthday.

equal C–S bond lengths (1.665(3) and 1.679(3) Å) as a consequence of negative charge delocalization. The S–C–S angle of 127.4(2)° is comparable to those found in carboxylate betaines,⁵ although the atomic radius of sulfur is larger than that of oxygen. However, the C–C–S angles are markedly different (121.1(2) and 111.6(2)°).

In compound **1** the *α*-H atoms of the pyridyl ring are activated by the positive charge on the N atom and have a tendency to form weak hydrogen bonds of the type C–H...X (X = O, S). In the crystal structure of **1**, a pair of centrosymmetrically-related molecules are joined by two C–H...S hydrogen bonds (H(5AA)...S(1) 2.894 Å, C(5A)–H(5AA)...S(1) 164.1°, H(5AA)...S(1)–C(7) 133.8°; C(5A)–H(5AA)...S(1)–C(7) torsion angle 39.2°) to form a dimer with a central 12-membered ring (Fig. 1). Furthermore, adjacent dimers, whose mean planes make a dihedral angle of 26.1°, are interconnected through the formation of C–H...S hydrogen bonds (H(1AB)...S(2) 2.927 Å, C(1B)–H(1AB)...S(2) 155.4°, H(1AB)...S(2)–C(7) 87.6°; C(1B)–H(1AB)...S(2)–C(7) torsion angle –107.7°), thus leading to a corrugated layer matching the (100) face, and the crystal structure consists of a stack of layers with an inter-layer spacing of $a \cdot \sin \beta = 10.316$ Å. The C–H...S hydrogen bond lengths and angles are in good agreement with those found in *meso*-tetraphenyldithiasapphyrin (C–H...S 2.91 Å, 131.2°; 3.16 Å, 131.2°).⁶

Ligand **1** does not easily coordinate to a metal atom, and the cadmium(II) complex Cd(pydta)₂Cl₂ **2** is thus far the only one to be successfully synthesized and characterized by X-ray crystallography. The molecular structure and atomic numbering scheme of **2** are shown in Fig. 2, and selected bond lengths and bond angles are displayed in Table 1. In the discrete molecule, the Cd(1) atom is in a distorted square-pyramidal CdS₃Cl₂ environment, with atom Cl(2) at the apex, which is similar to the CdO₃L₂ coordination mode found in [CdL₂L₂] (L = Ph₃P⁺(CH₂)₃CO₂[–]).⁷ Of the two independent dithiocarboxylate betaine ligands, one acts in an essentially symmetric chelate mode [Cd–S 2.707(1), 2.742(2) Å, Cd–S–C 85.7(2), 86.5(2)°], whereas the other occupies one coordination site with a much shorter Cd–S bond length of 2.552(2) Å. The symmetric chelate mode of the dithiocarboxylate group is commonly found in cadmium(II) dithiocarbamate complexes such as [NEt₄][Cd(S₂CNEt₂)₂(NCS)]⁸ and [PPh₄][Cd(S₂CNEt₂)₂X] (X = Br, Cl)⁹ (Cd–S distances in the range of 2.571–2.731 Å), although it is relatively rare among metal carboxylates. This difference may be ascribed to the fact that the Cd–S bond distance is longer

than the Cd–O distance, which leads to a less crowded coordination sphere. The conclusion that relative bulkiness of co-existing ligands in the coordination sphere of the metal dictates the ligation mode of the dithiocarboxylate group is also supported by the observation that in zinc(II) dithiocarbamates the dithiocarboxylate group commonly acts in the asymmetric chelate mode, as found in [NEt₄][Zn(S₂CNEt₂)₂(NCS)] (Zn–S 2.319(2), 2.672(3); 2.325(4), 2.591(1)),⁸ [Me³PrNCS]₂Zn·Me₂N(CH₂)₂NMe₂ and [Me³PrNCS]₂Zn·C₅H₅N (shorter Zn–S bonds in the range 2.3362(7)–2.3498(7) Å; longer bonds in the range 2.586(2)–2.6103(7) Å).¹⁰ In addition, if vectors are drawn from the Cd(II) atom to the carbon atoms of the dithiocarboxylate groups in **2**, the angles between each vector and the Cd–Cl bonds lie in the range 102.6–116.3°, which are close to the value 109.3° for a regular tetrahedron. This implies that the cadmium(II) atom, having a spherical d¹⁰ electronic configuration, tends to interact with as many ligands as possible to lower the energy of the system, while striving to attain an ideal coordination environment to reduce the repulsion between the ligands. The occurrence of both mono- and bi-dentate coordination modes of the independent dithioacetate ligands in **2** may thus be accounted for on this basis.

In the crystal structure of **2**, the pendent sulfur atom S(4) and ligating sulfur atom S(1), which is less strongly bound to the metal center as compared to S(2) and S(3) (see Table 1), form acceptor C–H...S hydrogen bonds (H...S 2.886 Å, C–H...S 165.9°; H...S 2.886 Å, C–H...S 131.2°) with the pyridyl rings belonging to neighboring molecules. In addition, each chloro ligand forms three C–H...Cl hydrogen bonds with the methylene groups and pyridyl rings from three adjacent molecules (H...Cl(1) 2.695, 2.766, 2.741 Å; C–H...Cl(1) 154.0, 128.2, 147.8°; H...Cl(2) 2.806, 2.748, 2.713 Å; C–H...Cl(2) 163.8, 147.9, 159.6°), thus generating a three-dimensional network (Fig. 3).

Hydrogen bonding interactions have been extensively studied in biosystems¹¹ and in the development of supramolecular chemistry.¹² The most common hydrogen bonds are of the type A–H...B where A and B can be either O and N. However, in the absence of such strong hydrogen-bonding interactions, various types of weak intermolecular cohesion such as π – π interaction, C–H... π , and C–H...X (X = halogen atom) hydrogen bonds play a dominant role in determining the molecular packing in crystals.^{11c,13} Although there are many examples of supermolecules held together by C–H...O and C–H...N hydrogen bonds, the assembly of molecular aggregates by C–H...S hydrogen bonds have not been exploited

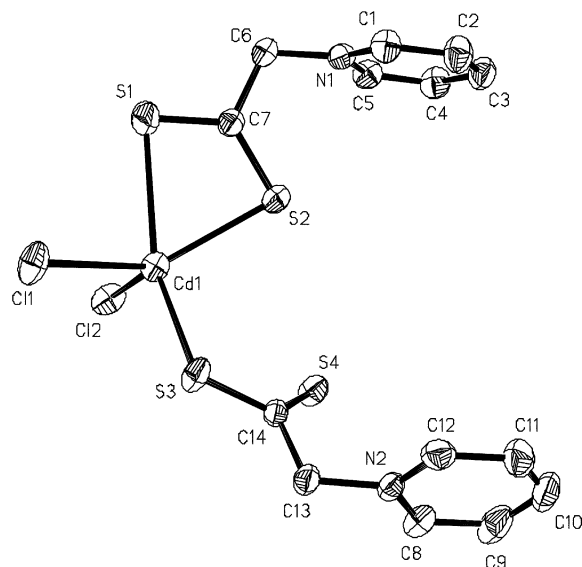


Fig. 2 Perspective view (35% thermal ellipsoids) of [Cd(pydta)₂Cl₂] **2** with atomic numbering scheme.

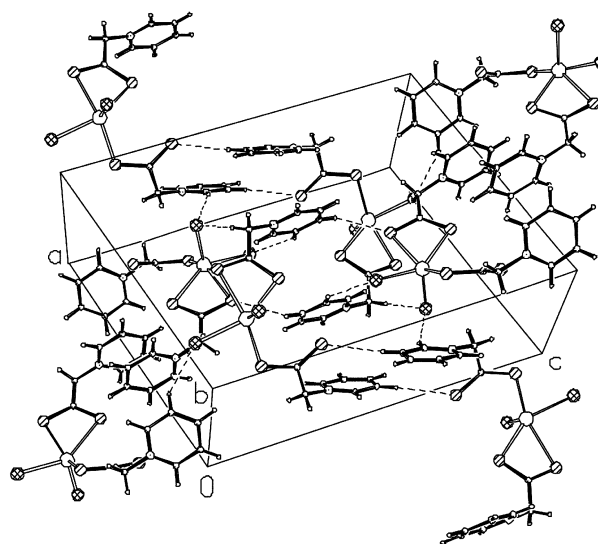


Fig. 3 Molecular packing in the crystal structure of [Cd(pydta)₂Cl₂] **2**. The C–H...S and C–H...Cl hydrogen bonds are indicated by broken lines.

until quite recently.^{6,14} Compound **1** provides an example of an organic solid consolidated by C–H···S hydrogen bonding, and complex **2** features an interplay of intermolecular C–H···S and C–H···Cl interactions in stabilizing the molecular packing of a neutral coordination compound.

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Notes and references

‡ Pyridinodithioacetate (pydta) **1** was prepared according to the literature method.⁴ Orange prismatic crystals suitable for X-ray structure analysis were obtained from recrystallization in DMF at –15 °C.

[Cd(pydta)₂Cl₂] **2**: ligand **1** (676 mg, 4.0 mmol) and cadmium(II) chloride (366 mg, 2.0 mmol) were dissolved in distilled water–methanol (v/v = 2 : 1). The solution was adjusted to pH 4 using 2 M hydrochloric acid. The resulting yellow solution was filtered, and yellow prismatic crystals were obtained by allowing the filtrate to stand for several days at ambient temperature. Anal. Calc. for (C₇H₇NS₂)₂CdCl₂: C, 32.23, H, 2.68; N, 5.36. Found: C, 32.19; H, 2.62; N, 5.33%.

X-Ray crystallography: diffraction data were collected at 293 K with Mo-K α radiation ($\lambda = 0.71073$ Å) on a Rigaku RAXIS IIC image-plate for **1** (rotating anode, 50 kV, 90 mA, $2\theta_{\max} = 52^\circ$, oscillation range from 0 to 155°, $\Delta\phi = 5^\circ$, 31 frames),¹⁵ and on a Siemens P4/PC diffractometer for **2** ($2\theta_{\max} = 60^\circ$). Empirical absorption correction (max. and min. transmission 1.216 and 0.715) based on Fourier coefficient fitting using the ABCOR program¹⁶ was applied for **1**, and that (max. and min. transmission 1.00 and 0.80) based on ψ -scan was applied for **2**. The structures were solved by direct methods, and all non-hydrogen atoms were subject to anisotropic refinement using the SHELXTL program package.¹⁷ *Crystal data* for **1**: C₇H₇NS₂, $M = 169.26$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.440(2)$, $b = 7.787(2)$, $c = 10.037(2)$ Å, $\beta = 98.89(3)^\circ$, $V = 806.2(3)$ Å³, $Z = 4$, $D_c = 1.395$ g cm⁻³, $\mu = 0.576$ cm⁻¹. Full-matrix least-squares refinement on F^2 (1430 unique data, 92 variables) converged to $R1 = 0.065$ for 1320 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.188$ for all data. *Crystal data* for **2**: C₁₄H₁₄N₂S₄CdCl₂, $M = 521.81$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.301(3)$, $b = 8.209(6)$, $c = 18.014(3)$ Å, $\beta = 101.86(1)^\circ$, $V = 1925(2)$ Å³, $Z = 4$, $D_c = 1.801$ g cm⁻³, $\mu = 1.844$ cm⁻¹. Full-matrix least-squares refinement on F^2 (5347 unique data, 208 variables) converged to $R1 = 0.049$ for 3584 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.120$ for all data.

CCDC reference numbers 121647 and 121648.

See <http://www.rsc.org/suppdata/dt/b3/b301639k/> for crystallographic data in CIF or other electronic format.

- (a) R. Selvaraju, M. Manoharan, P. Laavanya, K. Panchanatheswaran and P. Venunalingam, *J. Chem. Res. (S)*, 1999, 82; (b) I. Miyashita, K. Matsumoto, M. Kobayashi, A. Nagasawa and J. Nakayama, *Inorg. Chim. Acta*, 1998, **283**, 256; (c) S. Bhattacharyya, S. B. Kumar, S. K. Dutta, E. R. T. Tiekink and M. Chaudhury, *Inorg. Chem.*, 1996, **35**, 1967; (d) K. Shinzi, K. Nobuyuki, N. Osamu, K. Yuka, K. Takahiro and E. Masahiro, *Inorg. Chem.*, 1999, **38**, 496; (e) F. R. Larry, F. Juan, M. Antonio, N. Rafael, S. Violeta and V. Pablo, *Inorg. Chem.*, 1997, **36**, 6166; (f) G. D. Thorn, R. A. Ludwig, *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam, 1962.

- (a) W. O. Foye and S. J. Chatterji, *Pharm. Sci.*, 1996, **85**, 810; (b) W. O. Foye, R. W. Jones, P. K. Ghoshal and B. Almassian, *J. Med. Chem.*, 1987, **30**, 57; (c) W. O. Foye and J. M. Kauffman, *J. Pharm. Sci.*, 1979, **68**, 336; (d) W. O. Foye, Y. J. Lee, K. A. Shah and J. M. Kauffman, *J. Pharm. Sci.*, 1978, **67**, 962; (e) H. J. Bestmann, R. Engler, H. Hartung and K. Roth, *Chem. Ber.*, 1979, **112**, 28; (f) R. Gompper, B. Wetzel and W. Elser, *Tetrahedron Lett.*, 1968, 5519.
- (a) D.-D. Wu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1998, 367; (b) P.-R. Wei, T. C. W. Mak and D. A. Atwood, *Inorg. Chem.*, 1998, **37**, 2605; (c) S.-L. Li and T. C. W. Mak, *Struct. Chem.*, 1997, **8**, 49; (d) D.-D. Wu and T. C. W. Mak, *Polyhedron*, 1996, **15**, 655; (e) S.-L. Li and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1995, 1519; (f) P.-W. Wei, D.-D. Wu, B.-M. Wu, Z.-Y. Zhang and T. C. W. Mak, *J. Chem. Crystallogr.*, 1997, **27**, 609 and references therein.
- F. Kröhnke and K. Gerlach, *Chem. Ber.*, 1962, **95**, 1108.
- S.-L. Li and T. C. W. Mak, *J. Mol. Struct.*, 1996, **380**, 135.
- S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, A. Vij and R. Roy, *Angew. Chem., Int. Ed.*, 1998, **37**, 3394.
- S.-L. Li and T. C. W. Mak, *Polyhedron*, 1997, **16**, 199.
- R. Baggio, A. Frigerio, E. B. Halac, D. Vega and M. Perec, *J. Chem. Soc., Dalton Trans.*, 1992, 549.
- R. Baggio, M. T. Garland and M. Perec, *Acta Crystallogr., Sect. C*, 1996, **52**, 823.
- M. A. Malik, M. Motevalli, P. O'Brien and J. R. Walsh, *Inorg. Chem.*, 1997, **36**, 1263.
- (a) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997; (b) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991; (c) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, New York, 1999.
- (a) N. B. Bowden, M. Weck, I. S. Choi and G. M. Whitesides, *Acc. Chem. Res.*, 2001, **34**, 231; (b) K. Choi and A. D. Hamilton, *J. Am. Chem. Soc.*, 2001, **123**, 2456; (c) L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem., Int. Ed.*, 2001, **40**, 2382; (d) M. C. T. Fyfe and J. F. Stoddart, *Acc. Chem. Res.*, 1997, **30**, 393–401; (e) C. B. Åakeroy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397; (f) S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; (g) P. A. Gale, *Coord. Chem. Rev.*, 2000, **199**, 181.
- (a) C. A. Hunter, *Chem. Soc. Rev.*, 1994, 101; (b) T. Steiner, J. A. Kanters and J. Kroon, *Chem. Commun.*, 1996, 1277; (c) T. Steiner, *Chem. Commun.*, 1997, 727; (d) G. Harakas, T. Vu, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1998, **120**, 6405; (e) M. J. Zaworotko and K. Biradha, *J. Am. Chem. Soc.*, 1998, **120**, 6431; (f) I. Unamuno, J. M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, R. Calvo and T. Rojo, *Inorg. Chem.*, 1988, **37**, 6452; (g) P. K. Thallapally and A. Nangia, *CrystEngComm.*, 2001, **27**, 114; (h) L. Brammer, E. A. Bruton and P. Sherwood, *Cryst. Growth. Des.*, 2001, **1**, 277; (i) M. Nishio, M. Hirota and Y. Umezawa, *The CH π Interaction: Evidence, Nature, and Consequences*, Wiley-VCH, New York, 1998.
- (a) M. J. Potrzebowski, M. Michalska, A. E. Koziol, S. Kazmierski, T. Lis, J. Pluskowski and W. Ciesielski, *J. Org. Chem.*, 1998, **64**, 4209; (b) H. Borrmann, I. Persson, M. Sandström and C. M. V. Stålhandske, *J. Chem. Soc., Perkin Trans. 2*, 2000, 393; (c) A. D. Bond and W. Jones, *J. Chem. Soc., Dalton Trans.*, 2001, 3045.
- (a) J. Tanner and K. L. Krause, *Rigaku J.*, 1994, **11**, 4; J. Tanner and K. L. Krause, *Rigaku J.*, 1990, **7**, 28; (b) K. L. Krause and G. N. Phillips, *Appl. Crystallogr.*, 1992, **25**, 1446.
- T. Higashi, *Rigaku Corporation*, Tokyo, © 1995.
- G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.