

relaxed until the final minimum was reached. No anisotropic displacement parameters can be applied and, due to systematic measurement errors, several isotropic displacement parameters remain physically non-reasonable, *i.e.* close to zero. Final difference Fourier maps display residual peaks. The label and distance of the closest atom sites are D260/0.71 Å and C33/0.98 Å for the 1/4 and 1/5 phases, respectively.

For both compounds, data reduction: *COLL5* (Lehmann & Larsen, 1974); program(s) used to refine structures: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1994); software used to prepare material for publication: *CRYSTALS*.

One of us (OH) is financially supported by the 'Ministère Français de l'Enseignement Supérieur et de la Recherche'. We are very grateful to J.-M. Godard (Laboratoire de Physique des Solides, Université Paris XI Paris-Sud, France) for the elaboration of the sample and to P. Fouilloux for his technical support during the experiment at the Orphée reactor. Stimulating discussions with Drs A. Goukassov and M. Quilichini (LLB, CEA/Saclay, France), and with Professor J. M. Pérez-Mato (DFMC, UPV, Bilbao, Spain) are gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1472). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Ezpeleta, J. M., Zúñiga, F. J., Paulus, W., Cousson, A., Hlinka, J. & Quilichini, M. (1996). *Acta Cryst.* **B52**, 810–816.
- Ezpeleta, J. M., Zúñiga, F. J., Pérez-Mato, J. M., Paciorek, W. & Breczewski, T. (1992). *Acta Cryst.* **B48**, 261–269.
- Hernandez, O., Hlinka, J. & Quilichini, M. (1996). *J. Phys.* **1 (Fr.)**, **6**, 231–236.
- Hernandez, O., Quilichini, M., Pérez-Mato, J. M., Zúñiga, F. J., Dušek, M., Kiat, J.-M. & Ezpeleta, J. M. (1999). *Phys. Rev. B*. Accepted.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- Pérez-Mato, J. M. (1988). *Solid State Commun.* **67**, 1145–1150.
- Pérez-Mato, J. M. (1991). *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. Pérez-Mato, F. J. Zúñiga & G. Madariaga, pp. 117–128. Singapore: World Scientific.
- Sears, V. F. (1992). *Neutron News*, **3**, 26–37.
- Unruh, H. G., Hero, F. & Dvorak, V. (1989). *Solid State Commun.* **70**, 403–408.
- Watkin, D. J., Prout, C. K., Carruthers, R. J. & Betteridge, P. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.
- Zúñiga, F. J., Ezpeleta, J. M., Pérez-Mato, J. M., Paciorek, W. & Madariaga, G. (1991). *Phase Transitions*, **31**, 29–43.

Acta Cryst. (1999). **C55**, 1466–1470

Polymorphs of [(2*S*,3*S*)- α -Me-*N,N'*-bis-(salicylidene)butane-2,3-diaminato]bis-(pyridine)cobalt(III) tetrafluoroborate hydrate

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(Received 20 April 1998; accepted 14 May 1999)

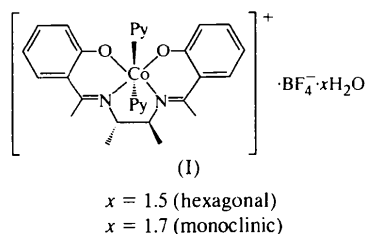
Abstract

The title compound, {2,2'-[butane-2,3-diylbis(nitrilo-1-ethylidene)diphenolato-*O,N,N',O'*]bis(pyridine-*N*)-cobalt(III) tetrafluoroborate hydrate, [Co(C₂₀H₂₂N₂O₂)(C₅H₅N)₂]BF₄·xH₂O or [Co{ α -Me-sal₂-(*S,S*)-bn}(py)₂]·BF₄·xH₂O (py is pyridine), showed polymorphs of crystals grown at the same time; one crystallized in the hexagonal system ($x = 1.5$) with a very long *c* axis and the other was in the monoclinic system ($x = 1.7$). The cell axes of the two structures were related simply to each other by $a_m \simeq a_h$, $b_m \simeq a_h + 2b_h$ and $c_m \simeq c_h/2$, where the axes of the hexagonal and monoclinic cells are identified by subscripts *h* and *m*, respectively. The complex cations, as well as the molecular arrangements in both structures, are quite similar to each other. The cation adopts octahedral coordination formed by the tetradentate salen-type Schiff base ligand in the basal plane and two *trans* pyridine ligands. The cation has an approximate twofold axis of rotation through the Co atom. The two methyl groups of the C—C bridge take an antiperiplanar conformation. The counter-ion is located nearly in the basal plane of the cation. The cations form dimers *via* π – π stacking between pyridine rings. Layers of cation dimers and anions stack alternately along *c*. The hexagonal structure includes 1.5 water molecules per Co atom and the monoclinic structure has 1.7 water molecules.

Comment

The molecular design of chiral tetradentate Schiff base complexes of manganese(III) and cobalt(III) is of great interest in the development of enantioselective oxygenation or hydrogenation catalysts for olefins or ketones (Jacobsen, 1993, and references therein; Katsuki, 1995; Nagata *et al.*, 1995; Bernardo *et al.*, 1996; Lam *et al.*, 1996). In the course of our investigation of Co^{III} complexes with chiral salen-type Schiff base ligands,

the title compound, (I), was prepared. In a preliminary check of the crystals prior to data collection, a polymorphism of the compound was occasionally found. The crystals of the two polymorphs are quite similar in colour, as well as in crystal habit (hexagonal plates). Therefore, it was very difficult to distinguish them optically.



The molecular structures and packing features of both crystals closely resemble each other and numerical results (Table 1) are given only for the hexagonal structure. The coordination around the Co atom is a slightly distorted octahedron (Fig. 1*a*). The salen-type Schiff base lies in the basal plane as is commonly observed. The methyl groups on the C—C bridge (bn-Me) take antiperiplanar axial configurations owing to

the steric effects of the α -methyl groups. The py ligands coordinate at *trans* positions with a coplanar disposition; their mean plane is almost perpendicular to the plane of the salen-type moiety. Thus, the cation has an approximate twofold axis of rotation through the midpoints of the basal N···N and O···O lines, though the py rings, as well as the salen basal plane, are slightly affected by repulsion from the bn-Me groups (see Fig. 1*b*). The coplanarity of the py rings and the axial configuration of the bn-Me groups are distinct differences in comparison with a related salen compound with no α -Me (Fukuda *et al.*, 1997), in which the bn-Me groups take equatorial configurations and the py rings are twisted with respect to each other by about 90° .

The complex cations form dimers through π - π stacking between py rings, as shown in Fig. 1*b*). In the hexagonal structure, the dimers have a twofold axis at $z = \frac{1}{12}$ and its equivalents; in the monoclinic structure, adjacent cations, related by the twofold axis at $z = \frac{1}{2}$ and its equivalents, are paired to form dimers. Thus, six cation dimers exist in both unit cells. The packing of the cations are shown in Fig. 2. The counter-ion is located nearly in the salicyl skeletal plane. The structures consist of alternate stacking of layers of cation dimers and

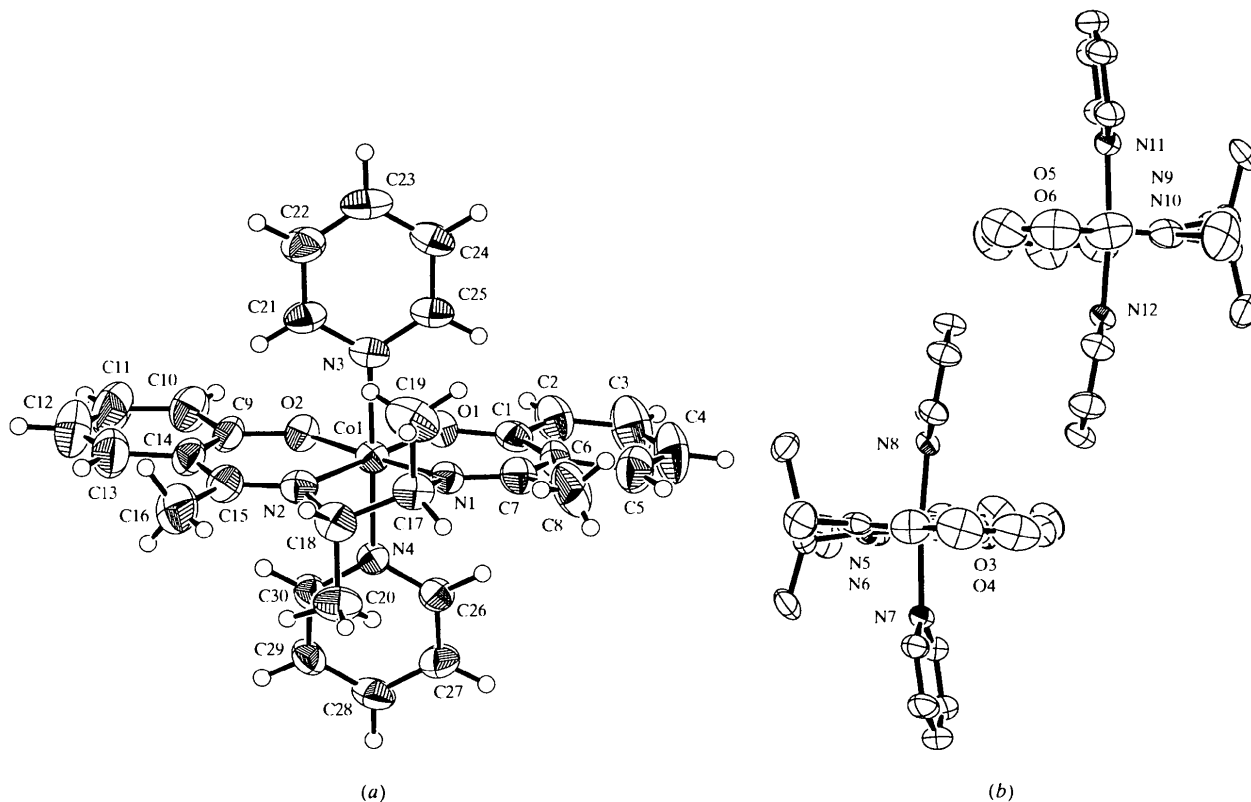


Fig. 1. (a) The complex cation of the hexagonal structure and (b) an example of the cation dimerization in the monoclinic structure. The displacement ellipsoids are drawn at the 40% probability level.

anions along *c*. A water molecule is bonded to each of the salen moieties through O—H...O hydrogen bonds (O3W in the hexagonal structure, and O7W, O8W and O9W in the monoclinic one). All the water molecules might also be linked by hydrogen bonds to each other.

The molecular arrangement along *c* in the hexagonal structure is of an infinite helical type owing to the 6_5 screw axis. In the monoclinic cell, there are two such equivalent chains running separately along *c* but with only a half unit of the hexagonal period, reflecting the difference between lattice spacings of *c* axes. One of the three anions was very much disordered around two sites; one shows a rotational disorder around a B—F bond on a twofold axis, while the other is positionally disordered near another twofold axis. The *c/a* ratio in the hexagonal cell is unusually large at about 9.73, and the material has a layer structure. Alcock & Hough (1972) argued on a layered tetragonal structure with an unusual long cell [*c/a* = 9.91; 3,3'-methylenebis(6-bromo-4-hydroxycoumarin)] that co-existence of high-order screw and twofold axes are essential to cause such layered stacking of molecules, since the molecular interaction was fairly weak along *c* but strong in the *xy* plane. Since short contacts in the *xy* plane are not found and the twofold axes contribute directly to the dimerization, this seems not to be the case for the present compound.

If the *b* direction of every alternate cell in the monoclinic structure is reversed, by 180° around the *a* axis for example, the resulting hypothetical structure closely resembles the hexagonal one, as can be seen in Fig. 2, though there remains an ambiguity of the atomic *y* coordinates. The disordered anions mentioned above are located in or near (001), which is the boundary plane of this reversal operation. Therefore, the anion might play a role in the crystallization of the compound; that is, if the anion is ordered, the crystal takes the hexagonal structure which is probably more stable than the monoclinic one.

The present work on the hexagonal structure succeeded as a test study on the structure determination by means of four-circle diffractometry of a crystal with an extremely long axis.

Experimental

The title compound was synthesized by the addition of an aqueous solution (10 ml) of pyridine (2.45 g, 0.031 mol) and NaBF_4 (3.4 g, 0.031 mol) to a mixture of a chloroform solution (10 ml) of α -Me-sal₂-(*S,S*)-bnH₂ [1.0 g, 3.1 mmol; the Schiff base ligand was prepared from α -methylsalicylaldehyde and (2*S,3S*)-butanediamine in methanol-chloroform, and the chiral diamine was resolved by a modification of a literature

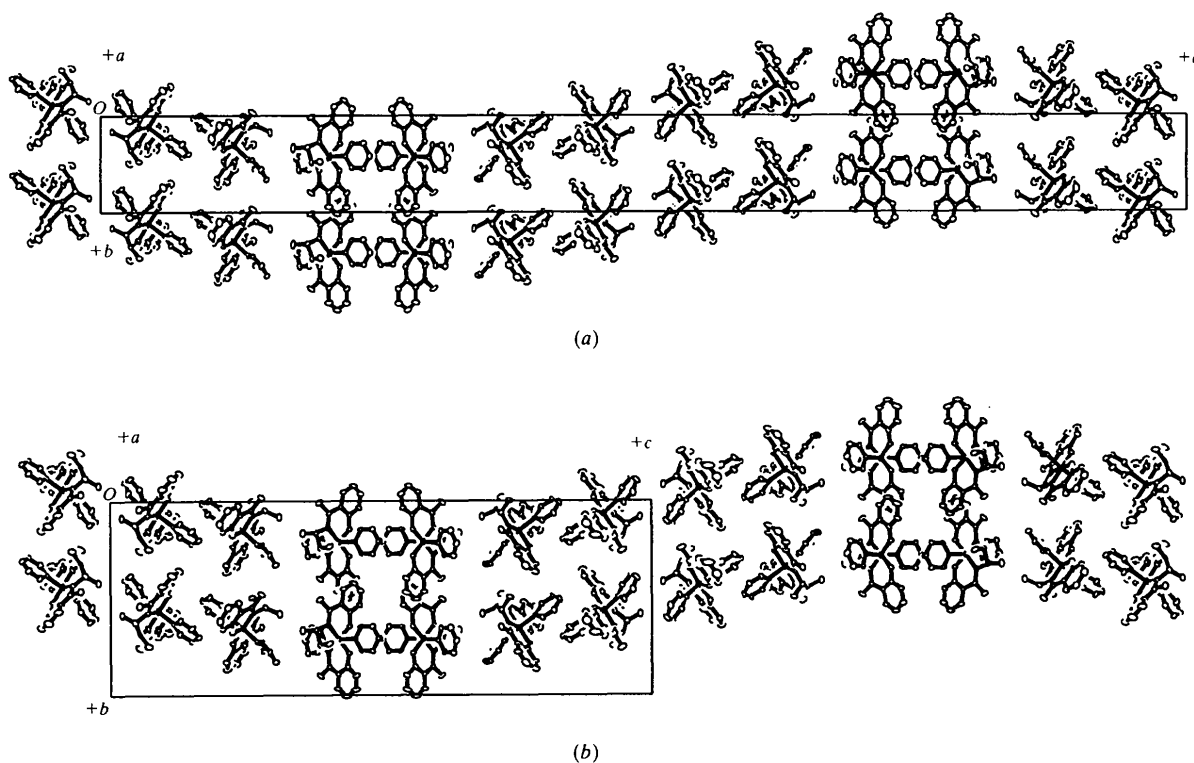
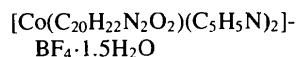


Fig. 2. A comparison of cation arrangements (a) in the hexagonal structure and (b) in a hypothetical one based on the monoclinic cell (enclosed by cell edges). The structure (b) is constructed by stacking of the monoclinic cells alternately with +*a* and -*a* directions along *c*. H atoms have been omitted for clarity.

method (Dickey *et al.*, 1952)] and a methanol solution (10 ml) of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.78 g, 0.031 mol) under argon, followed by passing air for 12 h to give dark-brown crystals ($\Delta\epsilon_{603} = +9.47 \text{ mol}^{-1} \text{ dm}^{-3} \text{ cm}^{-1}$ in methanol containing an excess of pyridine). Crystals suitable for single-crystal X-ray structure analysis were grown by slow evaporation of a methanol solution of the complex.

Compound (I) in the hexagonal system

Crystal data



$M_r = 653.2$

Hexagonal

$P6_522$

$a = 10.422$ (6) Å

$c = 101.433$ (7) Å

$V = 9541$ (8) Å³

$Z = 12$

$D_x = 1.36 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Rigaku AFC-5R diffractometer

ω scans

Absorption correction:

analytical (de Meulenaer & Tompa, 1965)

$T_{\min} = 0.170$, $T_{\max} = 0.298$

13 193 measured reflections

6231 independent reflections (plus 68 Friedel-related reflections)

Refinement

Refinement on F

$R = 0.054$

$wR = 0.059$

$S = 1.892$

3903 reflections

390 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o) + 0.00027|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.44 \text{ e Å}^{-3}$

$\Delta\rho_{\min} = -0.13 \text{ e Å}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.5418$ Å

Cell parameters from 25

reflections

$\theta = 25.9$ – 28.5°

$\mu = 4.77 \text{ mm}^{-1}$

$T = 298.2$ K

Hexagonal plate

$0.60 \times 0.50 \times 0.30$ mm

Dark brown

3903 reflections with

$I > 1.5\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 72.5^\circ$

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 10$

$l = 0 \rightarrow 125$

4 standard reflections

every 150 reflections

intensity decay: 3.2%

Extinction correction:

Zachariasen (1967) type

2 Gaussian isotropic

Extinction coefficient:

0.009 (2)

Scattering factors from

International Tables for

Crystallography (Vol. C)

Absolute structure: see

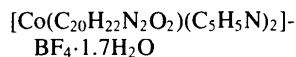
below

Flack parameter = 0.003 (3)

(Flack, 1983)

Compound (I) in the monoclinic system

Crystal data



$M_r = 657.3$

Monoclinic

$C2$

$a = 10.305$ (2) Å

$b = 18.047$ (3) Å

$c = 50.764$ (2) Å

$\beta = 92.463$ (9) $^\circ$

$V = 9432$ (2) Å³

$Z = 12$

$D_x = 1.39 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Rigaku AFC-5R diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (North *et al.*, 1968)

$T_{\min} = 0.74$, $T_{\max} = 0.86$

16 927 measured reflections

16 139 independent

reflections

(plus 788 Friedel-related

reflections)

Refinement

Refinement on F

$R = 0.056$

$wR = 0.069$

$S = 2.990$

14 486 reflections

1152 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.057$

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25

reflections

$\theta = 18.5$ – 19.8°

$\mu = 0.609 \text{ mm}^{-1}$

$T = 298.2$ K

Hexagonal plate

$0.50 \times 0.35 \times 0.25$ mm

Dark brown

13 942 reflections with

$F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 27.5^\circ$

$h = 0 \rightarrow 13$

$k = -23 \rightarrow 19$

$l = -65 \rightarrow 65$

4 standard reflections

every 150 reflections

intensity decay: 1.2%

$\Delta\rho_{\max} = 0.89 \text{ e Å}^{-3}$

$\Delta\rho_{\min} = -0.44 \text{ e Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Absolute structure: see

below

Flack parameter = 0.05 (1)

(Flack, 1983)

Some methyl and water H atoms were found in difference syntheses; other cationic H atoms were located by geometrical calculations [C—H = 0.95 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$]. The water molecules are distributed in several positions; the distributions are not the same but similar in both structures. Some water molecules were refined to be less than unit occupancy; 1.5 water molecules are included per Co atom in the hexagonal structure, (1), and 1.7 molecules are included in the monoclinic structure, (2). The water H atoms were not determined.

In (1), the hexagonal cell had an extremely elongated c axis. Therefore, the intensity measurement was made using an ω -scan technique with Cu $K\alpha$ radiation. A relatively large crystal which showed sharp diffraction peaks was selected for data collection because weakness of high-angle intensities and difficulty in resolving neighbouring reflections were expected, as are commonly observed for crystals with large cell dimensions. Even with a narrow receiving slit ($1 \times 0.75^\circ$) and small scan widths, however, resolution of the neighbouring peaks was insufficient for some reflections at special settings, as indicated, for example, by very unbalanced

Table 1. Selected geometric parameters (Å, $^\circ$) for (I) in the hexagonal system

Co1—O1	1.867 (3)	Co1—N2	1.916 (5)
Co1—O2	1.866 (4)	Co1—N3	1.994 (4)
Co1—N1	1.904 (4)	Co1—N4	1.993 (4)
O1—Co1—O2	83.5 (2)	O2—Co1—N4	87.5 (2)
O1—Co1—N1	94.5 (2)	N1—Co1—N2	87.6 (2)
O1—Co1—N2	177.8 (2)	N1—Co1—N3	90.7 (2)
O1—Co1—N3	87.2 (2)	N1—Co1—N4	94.2 (2)
O1—Co1—N4	89.2 (2)	N2—Co1—N3	93.7 (2)
O2—Co1—N1	177.3 (2)	N2—Co1—N4	89.8 (2)
O2—Co1—N2	94.5 (2)	N3—Co1—N4	174.1 (2)
O2—Co1—N3	87.5 (2)		

or high background(s); these reflections showed larger or smaller structure amplitudes than those of the equivalents. The deviations were up to several ten percent of the $|F_o|$ values in most cases and several hundred percent in extreme cases for weak reflections. Such reflections were mainly concentrated in a limited region of the reciprocal lattice space, *i.e.* $+h+k+l$ ($\theta = 10^\circ \rightarrow 50^\circ$ and $l = 10 \rightarrow 50$ depending on h and k); after they were removed (695 in total), the equivalent reflections were averaged and used for the structure determination. Owing to the mechanical blind regions of the diffractometer, 574 high-angle reflections ($62.5^\circ < \theta < 66^\circ$) could not be measured. The absorption correction was made by an analytical calculation using the crystal shape of the hexagonal plate. Water molecules were all isotropic. Large residual electron densities were not found in voids which could possibly contain some disordered water molecules.

In (2), the data collection was carried out first with an ω -scan technique using $\text{Cu K}\alpha$ radiation, and then with an $\omega/2\theta$ scan using $\text{Mo K}\alpha$ radiation, and finally some Bijvoet pairs were added to increase the number of reflections; thus, the effectiveness of the structure refinement gradually grew. The greatest problem, however, was the determination of the locations of the disordered anion near the (001) plane. A rigid group refinement was finally adopted for the positionally disordered anion formed by the B4, F13, F14, F15 and F16 atoms. In spite of prolonged calculations, the maximum Δ/σ ratio was not less than 0.06. The y coordinate of the Co atom was fixed in the structure refinement. Water molecules were disordered at several sites. These and the disordered anions were refined isotropically. Large residual electron densities were not found in voids.

The absolute structure in each case was determined from about 100 selected Bijvoet pairs with large differences, by refinement of the inverted structure to significantly higher residuals, and by refinement of the Flack (1983) parameter.

For both compounds, data collection: *MSCIAFC Diffractometer Control System* (Rigaku Corporation, 1991); cell reduction: *MSCIAFC Diffractometer Control System*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1272). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W. & Hough, E. (1972). *Acta Cryst.* **B28**, 1957–1960.
- Bernardo, K., Leppard, S., Robert, A., Commenges, G., Dahan, F. & Meunier, B. (1996). *Inorg. Chem.* **35**, 387–396.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Dickey, F. H., Fickett, W. & Lucas, H. L. (1952). *J. Am. Chem. Soc.* **74**, 944–951.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fukuda, T., Ishii, K., Nakano, Y. & Fujii, Y. (1997). Unpublished results.
- Jacobsen, E. N. (1993). *Catalytic Asymmetric Synthesis*, edited by I. Ojima, pp. 159–202. New York: VCH Publishers Inc.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Katsuki, T. (1995). *Coord. Chem. Rev.* **140**, 189–214.
- Lam, F., Xu, J. X. & Chan, K. S. (1996). *J. Org. Chem.* **61**, 8414–8418.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nagata, T., Yorozu, K., Yamada, T. & Mukaiyama, T. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2145–2147.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku Corporation (1991). *MSCIAFC Diffractometer Control System*. Rigaku Corporation, Tokyo, Japan.
- Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1999). **C55**, 1470–1472

A maleate-bridged dinuclear bipyridine-containing zinc(II) complex

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(Received 14 January 1999; accepted 17 May 1999)

Abstract

A novel cyclic dinuclear zinc complex with maleate dianions as the bridging ligands, di- μ -maleato-bis-[aqua(2,2'-bipyridine)zinc(II)] dihydrate, $[\text{Zn}_2(\text{C}_4\text{H}_2\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, has been characterized by X-ray analysis. The complex lies about a crystallographic inversion centre. The zinc centre has distorted square-pyramidal geometry with two bipy N atoms, a carboxylate O atom and an aqua O atom forming the base; the Zn—N bond lengths are in the range 2.1021 (15)–2.120 (2) Å and the Zn—O bond lengths are in the range 1.9709 (13)–2.125 (2) Å. A maleate O atom completes the coordination sphere in the apical site, with a Zn—O bond length of 2.0223 (13) Å. The Zn...Zn distance is 5.281 (1) Å.

Comment

Dinuclear zinc complexes with N- and O-donor ligands have been of considerable interest since such systems of two Zn atoms are known to exist at the active site of some zinc-containing enzymes, such as phospholipase