

Table 2. Geometric parameters (Å, °)

Ni—S(1)	2.453 (1)	Ni—S(2)	2.411 (1)
Ni—O(1)	2.035 (3)	Ni—O(31)	2.099 (4)
Ni—N(1)	2.139 (4)	Ni—N(2)	2.119 (4)
S(1)—C(7)	1.820 (6)	S(1)—C(8)	1.816 (6)
S(2)—C(9)	1.812 (6)	S(2)—C(10)	1.809 (6)
N(1)—C(1)	1.339 (6)	N(1)—C(5)	1.363 (6)
N(2)—C(12)	1.354 (7)	N(2)—C(16)	1.357 (7)
C(1)—C(2)	1.371 (7)	C(13)—C(14)	1.37 (2)
C(14)—C(15)	1.38 (1)	C(15)—C(16)	1.377 (8)
C(2)—C(3)	1.379 (8)	C(3)—C(4)	1.376 (9)
C(4)—C(5)	1.383 (7)	C(5)—C(6)	1.500 (7)
C(6)—C(7)	1.526 (8)	C(8)—C(9)	1.513 (9)
C(10)—C(11)	1.52 (1)	C(11)—C(12)	1.499 (8)
C(12)—C(13)	1.394 (8)		
S(1)—Ni—S(2)	87.41 (5)	S(1)—Ni—O(1)	94.9 (2)
S(1)—Ni—O(31)	171.9 (1)	S(1)—Ni—N(1)	91.7 (1)
S(1)—Ni—N(2)	84.6 (1)	S(2)—Ni—O(1)	174.7 (2)
S(2)—Ni—O(31)	98.8 (1)	S(2)—Ni—N(1)	84.6 (1)
S(2)—Ni—N(2)	92.7 (1)	O(1)—Ni—O(31)	79.3 (1)
O(1)—Ni—N(1)	90.6 (2)	O(1)—Ni—N(2)	92.3 (2)
O(31)—Ni—N(1)	94.0 (2)	O(31)—Ni—N(2)	89.9 (2)
N(1)—Ni—N(2)	175.5 (2)	C(7)—S(1)—C(8)	103.2 (3)
C(9)—S(2)—C(10)	101.7 (3)	C(1)—N(1)—C(5)	116.7 (4)
C(12)—N(2)—C(16)	117.0 (5)	S(1)—C(8)—C(9)	112.9 (4)
S(2)—C(9)—C(8)	113.7 (4)	S(2)—C(10)—C(11)	111.6 (5)
N(1)—C(1)—C(2)	124.5 (5)	C(1)—C(2)—C(3)	118.6 (5)
C(2)—C(3)—C(4)	118.4 (5)	C(3)—C(4)—C(5)	120.3 (5)
N(1)—C(5)—C(4)	121.5 (5)	N(1)—C(5)—C(6)	119.5 (4)
C(4)—C(5)—C(6)	118.9 (5)	C(5)—C(6)—C(7)	113.2 (4)
S(1)—C(7)—C(6)	110.2 (4)	C(10)—C(11)—C(12)	114.6 (6)
N(2)—C(12)—C(11)	119.5 (5)	N(2)—C(12)—C(13)	120.7 (6)
C(11)—C(12)—C(13)	119.8 (5)	C(12)—C(13)—C(14)	120.9 (6)
C(13)—C(14)—C(15)	118.9 (6)	C(14)—C(15)—C(16)	117.9 (6)
N(2)—C(16)—C(15)	124.5 (6)		

Data collection: Enraf-Nonius CAD-4 software. Data reduction: SDP (Frenz, 1978). Program used to solve structure: SHELXS86 (Sheldrick, 1986). Programs used to refine structure: SDP. Molecular graphics: SCHAKAL88 (Keller, 1988). The structure was solved by direct methods and subsequent difference Fourier methods. Anisotropic thermal parameters were refined for all non-H atoms. H atoms were included in the structure-factor calculations with  $B_{\text{iso}}$  fixed at  $4.00 \text{ \AA}^2$ .

We thank the DGICYT (Spain) for financial support (project PS88-0051).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71237 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1041]

## References

- Bermejo, E., Carballo, R., Castiñeiras, A., Lombao, A., Hiller, W. & Strähle, J. (1991). *Polyhedron*, **10**, 1579–1585.
- Castiñeiras, A., Carballo, R., Hiller, W. & Strähle, J. (1990). *Z. Kristallogr.* **193**, 251–259.
- Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
- Keller, E. (1988). *SCHAKAL88. Fortran Program for the Graphical Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.

- Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1993). **C49**, 1920–1923

## Structure of Diaquatetrakis( $\mu$ -2,6-difluorobenzoato- $\kappa$ O: $\kappa$ O')dicopper(II)

ANASTAS KARIPIDES\* AND CHARLOTTE WHITE

*Department of Chemistry, Miami University, Oxford, Ohio 45056, USA*

(Received 2 November 1992; accepted 27 April 1993)

## Abstract

The structure consists of centrosymmetric dimeric units,  $[\text{Cu}(\text{C}_6\text{H}_3\text{F}_2\text{COO})_2(\text{H}_2\text{O})]_2$ , formed from the bridging of pairs of copper(II) ions by carboxylate groups from four different 2,6-difluorobenzoate anions. The distorted octahedral coordination about each  $\text{Cu}^{\text{II}}$  ion consists of four carboxylate O atoms, a water molecule and a centrosymmetrically related copper ion. The  $\text{Cu}\cdots\text{Cu}$  distance is  $2.613 (1) \text{ \AA}$ . The most significant feature of the crystalline structure is the water-mediated coordination of one of the carbon-bound F atoms to the copper ion through a strong  $\text{C}-\text{F}\cdots\text{H}-\text{O}$  hydrogen bond [ $\text{F}\cdots\text{O}$   $2.962 (4) \text{ \AA}$ ,  $\text{F}\cdots\text{H}-\text{O}$   $163^\circ$ ]. Each 2,6-difluorobenzoate aryl group is twisted considerably from its corresponding carboxyl group plane [ $48.9, 104.2^\circ$ ].

## Comment

The structure determination of the title compound was carried out as part of a program to investigate the structural environments of carbon-bound F atoms in metal salts of fluorocarboxylic acids. Substitution of F atoms for hydrogen can often lead to structural motifs that are not possible with the corresponding hydrogen homolog. Thus, in fluorocarboxylate salts, carbon-bound F atoms have been found to participate in direct metal-ion binding ( $\text{C}-\text{F}\cdots\text{M}$ ) as well as indirect metal-ion binding through a water-mediated hydrogen bond ( $\text{C}-\text{F}\cdots\text{H}_2\text{O}-\text{M}$ ) (Murray-Rust, Stallings, Monti, Preston & Glusker, 1983; Karipides & Miller, 1984; Kulawiec & Crabtree, 1990).

The crystal structure consists of centrosymmetric dimeric units similar to those found in copper carboxylate structures (Brown & Chidambaram, 1973). The asymmetric unit includes two independent 2,6-difluorobenzoate groups designated (a) and (b),

one Cu atom and one water molecule. Each Cu atom is surrounded by four carboxylate O atoms from four different ligands, one water molecule and a centrosymmetrically related Cu<sup>II</sup> ion. The four carboxylate O atoms are essentially coplanar with the Cu atom displaced from this plane toward the water molecule by 0.19 Å. In the tetragonally distorted octahedron about each copper, the Cu<sup>II</sup>...Cu—O<sub>w</sub> grouping is almost linear [178.2(4)°] and the Cu—O<sub>w</sub> vector is essentially perpendicular (1.8°) to the plane of the four carboxylate O atoms. The range of Cu—O bond lengths of 1.949(2)–1.976(2) Å (carboxylate) and 2.146(2) Å (water), the mean bridging path length (Cu—O—C—O—Cu) 6.430(6) Å and the Cu...Cu distance of 2.613(1) Å are comparable with similar distances observed in aromatic and aliphatic copper(II) carboxylates (Harrison, Rettig & Trotter, 1972; Rao, Sathyanarayana & Manohar, 1983; Kawata *et al.*, 1992).

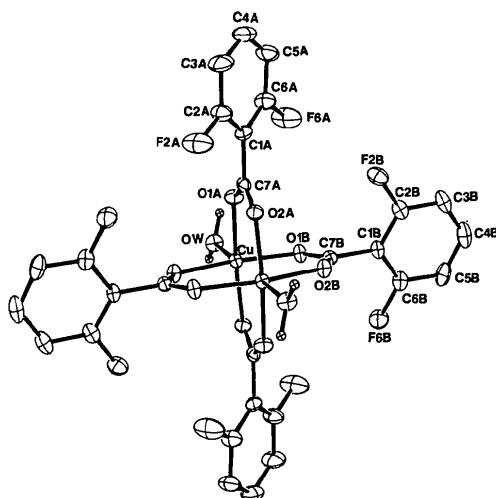


Fig. 1. A view of the structure showing the dimeric formula unit and the atom-labeling scheme. Aryl-ring H atoms have been omitted.

The crystalline structure is stabilized by hydrogen bonds involving the water molecule, the F atom, F2a, and the carboxylate O atom, O1b. The most significant feature of this structure is the presence of a strong intermolecular C—F...H—O<sub>w</sub> hydrogen bond. In a detailed study of the intermolecular interactions of the C—F bond, Murray-Rust *et al.* (1983) noted that F...O distances involved in hydrogen bonding should be less than 3.2 Å. The shortest previously reported F...O distances in C—F...H—O interactions include 3.00 Å observed in 9 $\alpha$ -fluorocortisol (Dupont, Dideberg & Campsteyn, 1972; Weeks, Duax & Wolff, 1973) and 2.995(2) Å in calcium 2-fluorobenzoate dihydrate (Karipides & Miller, 1984). To the best of our knowledge, the observed F...O<sub>w</sub> distance of 2.962(4) Å in the

present structure is the shortest F...O hydrogen-bond distance involving a carbon-bound F atom heretofore reported. Pertinent hydrogen-bonding parameters are given in Table 2. Although water molecules and carboxylate O atoms are the more likely donor groups toward metal ions in fluorocarboxylates, there is considerable crystallographic evidence that carbon-bound F atoms may participate in direct (C—F...M) metal-ion binding in structures of monovalent alkali-metal fluorocarboxylates (Murray-Rust *et al.*, 1983). The observed C—F...H—O—Cu bonding motif in copper(II) 2,6-difluorobenzoate hydrate is consistent with the premise (Karipides & Miller, 1984) that in divalent or trivalent metal-ion salts of fluorocarboxylic acids, indirect water-mediated coordination through a C—F...H<sub>2</sub>O—M hydrogen bond is more favorable than direct C—F...M binding.

In each of the 2,6-difluorobenzoate groups, (a) and (b), the plane of the aromatic ring is twisted considerably from the plane of the corresponding carboxylate group. These dihedral angles are 48.9 and 75.8° for (a) and (b), respectively. In calcium 2,6-difluorobenzoate dihydrate this angle is 48.2° (Karipides, White & Peiffer, 1992). Although the structure of free 2,6-difluorobenzoic acid has not been reported, we note that the twist angles in these 2,6-difluorobenzoate salts are considerably greater than the 29.8° found in pentafluorobenzoic acid, which contains fluorine substituents in the 2 and 6 positions (Benghiat & Leiserowitz, 1972).

## Experimental

### Crystal data

[Cu<sub>2</sub>(C<sub>7</sub>H<sub>3</sub>F<sub>2</sub>O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]

*M<sub>r</sub>* = 791.5

Triclinic

*P* $\bar{1}$

*a* = 7.404(1) Å

*b* = 10.006(1) Å

*c* = 10.093(1) Å

$\alpha$  = 90.28(1)°

$\beta$  = 97.68(1)°

$\gamma$  = 91.77(1)°

*V* = 740.64 Å<sup>3</sup>

*Z* = 1

*D<sub>x</sub>* = 1.774 Mg m<sup>-3</sup>

*D<sub>m</sub>* = 1.77 Mg m<sup>-3</sup>

Mo K $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25 reflections

$\theta$  = 8.35–17.25°

$\mu$  = 1.61 mm<sup>-1</sup>

*T* = 292 K

Prism

0.20 × 0.20 × 0.17 mm

Blue-green

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta/2\theta$  scans

Absorption correction:

empirical

*T<sub>min</sub>* = 0.9008, *T<sub>max</sub>* = 0.9974

2719 measured reflections

2572 independent reflections

2268 observed reflections

[*F* >  $\sigma$ (*F*)]

*R<sub>int</sub>* = 0.038

$\theta_{max}$  = 25.00°

*h* = -8 → 8

*k* = -11 → 11

*l* = 0 → 11

3 standard reflections

frequency: 210 min

intensity variation: none

## Refinement

Refinement on  $F^2$ Final  $R = 0.041$  $wR = 0.042$  $S = 1.15$ 

2268 reflections

217 parameters

H-atom parameters not refined

$$w = 1/[\sigma^2(F) + 0.0004F^2]$$

$$(\Delta/\sigma)_{\max} = 0.01$$

$$\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = 0.33 \text{ e } \text{Å}^{-3}$$

Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography*  
(1974, Vol. IV)

F2a—C2a—C3a	117.9 (4)	O2a <sup>i</sup> —Cu···Cu <sup>i</sup>	85.19 (7)
C1a—C2a—C3a	123.5 (4)	O1b—Cu—Ow	94.2 (1)
C2a—C3a—C4a	118.4 (4)	O1b—Cu···Cu <sup>i</sup>	86.18 (7)
C3a—C4a—C5a	120.7 (4)	O2b <sup>i</sup> —Cu—Ow	97.0 (1)
C4a—C5a—C6a	118.7 (4)	O2b <sup>i</sup> —Cu···Cu <sup>i</sup>	82.72 (7)
C5a—C6a—C1a	123.2 (4)	Ow—Cu···Cu <sup>i</sup>	178.2 (4)
F6a—C6a—C1a	118.4 (4)	Ow—H1w···F2a <sup>ii</sup>	163
F6a—C6a—C5a	118.3 (4)	Ow—H2w···O1b <sup>iii</sup>	160
C2b—C1b—C6b	116.0 (3)	H1w—Ow—H2w	106

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $1 + x, y, z$ ; (iii)  $1 - x, -y, -z$ .

The title compound was prepared from the stoichiometric reaction of 'basic' copper(II) carbonate,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , with a hot aqueous solution of 2,6-difluorobenzoic acid. Well formed crystals, which gave sharp optical extinction under crossed polarizers, were readily grown by slow evaporation of a filtered solution at ambient temperature.

The structure was solved using heavy-atom methods and refined by full-matrix least-squares procedures. H-atom positions were located from difference Fourier maps and adjusted along the corresponding C—H or O—H bond direction until the C—H and O—H bond lengths were 1.08 and 0.97 Å, respectively. However, H-atom coordinates and the fixed isotropic displacement parameter for each H atom were not refined.

Programs used include the Enraf-Nonius *SDP-Plus* program package (Frenz, 1985), a local version of *ORFLS* (Busing, Martin & Levy, 1962) and *ORTEPII* (Johnson, 1976).

AK thanks the National Institute of General Medical Sciences for financial support through grant GM40159-01 and the National Science Foundation (grant CHE-8418897) for funds to purchase the CAD-4 diffractometer system.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71283 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1050]

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ )

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Cu	0.15570 (5)	0.04618 (4)	-0.03114 (4)	0.0302
Ow	0.4090 (3)	0.1284 (3)	-0.0808 (3)	0.0477
O1a	0.0872 (3)	0.2111 (2)	0.0506 (3)	0.0454
O2a	-0.1827 (3)	0.1339 (2)	0.0988 (2)	0.0412
C7a	-0.0591 (4)	0.2226 (3)	0.0990 (3)	0.0360
F2a	-0.3832 (4)	0.3629 (3)	0.0478 (4)	0.111
F6a	0.1994 (4)	0.3560 (3)	0.2896 (4)	0.108
C1a	-0.0892 (5)	0.3536 (3)	0.1644 (4)	0.0432
C2a	-0.2517 (6)	0.4172 (4)	0.1386 (5)	0.0623
C3a	-0.2866 (7)	0.5360 (5)	0.1990 (6)	0.0810
C4a	-0.1548 (8)	0.5919 (5)	0.2907 (6)	0.0783
C5a	0.0079 (7)	0.5307 (5)	0.3238 (5)	0.0737
C6a	0.0381 (6)	0.4144 (4)	0.2580 (5)	0.0603
O1b	0.2629 (3)	-0.0149 (2)	0.1472 (2)	0.0400
O2b	-0.0060 (3)	-0.0873 (2)	0.2010 (2)	0.0398
C7b	0.1620 (4)	-0.0659 (3)	0.2257 (3)	0.0335
F2b	0.1426 (3)	0.0849 (2)	0.4564 (2)	0.0640
F6b	0.3712 (4)	-0.2924 (2)	0.2721 (3)	0.0706
C1b	0.2516 (4)	-0.1045 (4)	0.3618 (3)	0.0363
C2b	0.2359 (5)	-0.0289 (4)	0.4742 (4)	0.0475
C3b	0.3125 (6)	-0.0620 (5)	0.5996 (4)	0.0619
C4b	0.4123 (6)	-0.1755 (6)	0.6153 (5)	0.0723
C5b	0.4360 (6)	-0.2548 (5)	0.5070 (5)	0.0653
C6b	0.3535 (5)	-0.2164 (4)	0.3821 (4)	0.0484
H1w	0.4579	0.2049	-0.02693	0.0633
H2w	0.5094	0.0971	-0.1240	0.0633

Table 2. Selected geometry ( $\text{Å}, ^\circ$ )

Cu···Cu <sup>i</sup>	2.6127 (8)	C7b—O1b	1.259 (4)
Cu—O2a <sup>i</sup>	1.949 (2)	C7b—O2b	1.247 (4)
Cu—O1a	1.952 (2)	C1b—C7b	1.501 (4)
Cu—O2b <sup>i</sup>	1.966 (2)	C1b—C2b	1.380 (5)
Cu—O1b	1.976 (2)	C1b—C6b	1.370 (5)
Cu—Ow	2.146 (2)	C2b—C3b	1.362 (6)
C7a—O1a	1.255 (4)	C2b—F2b	1.351 (5)
C7a—O2a	1.255 (4)	C3b—C4b	1.373 (7)
C1a—C7a	1.500 (5)	C4b—C5b	1.381 (7)
C1a—C2a	1.373 (5)	C5b—C6b	1.387 (5)
C1a—C6a	1.368 (6)	C6b—F6b	1.366 (5)
C2a—C3a	1.380 (6)	Ow···F2a <sup>ii</sup>	2.962 (4)
C2a—F2a	1.344 (5)	Ow···O1b <sup>iii</sup>	2.870 (3)
C3a—C4a	1.357 (7)	H1w···F2a <sup>ii</sup>	2.02
C4a—C5a	1.370 (7)	H2w···O1b <sup>iii</sup>	1.94
C5a—C6a	1.376 (6)	Ow—H1w	0.97
C6a—F6a	1.346 (5)	Ow—H2w	0.97
O1a—C7a—O2a	125.8 (3)	F2b—C2b—C1b	117.3 (3)
O1a—C7a—C1a	117.4 (3)	F2b—C2b—C3b	119.2 (4)
O2a—C7a—C1a	116.7 (3)	C1b—C2b—C3b	123.4 (4)
C2a—C1a—C7a	122.9 (3)	C2b—C3b—C4b	118.5 (4)
C6a—C1a—C7a	121.7 (3)	C3b—C4b—C5b	121.2 (4)
O1b—C7b—O2b	126.0 (3)	C4b—C5b—C6b	117.5 (4)
O1b—C7b—C1b	116.8 (3)	C5b—C6b—C1b	123.3 (4)
O2b—C7b—C1b	117.2 (3)	F6b—C6b—C1b	116.9 (3)
C2b—C1b—C7b	121.7 (3)	F6b—C6b—C5b	119.8 (4)
C6b—C1b—C7b	122.3 (3)	O1a—Cu—Ow	96.6 (1)
C2a—C1a—C6a	115.4 (4)	O1a—Cu···Cu <sup>i</sup>	83.69 (7)
F2a—C2a—C1a	118.6 (4)	O2a <sup>i</sup> —Cu—Ow	96.6 (1)

## References

- Benghiat, V. & Leiserowitz, L. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 1778–1785.
- Brown, G. M. & Chidambaram, R. (1973). *Acta Cryst.* B29, 2393–2403.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Dupont, L., Dideberg, O. & Campstejn, H. (1972). *Acta Cryst.* B28, 3023–3032.
- Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- Harrison, W., Rettig, S. & Trotter, J. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1852–1856.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Karipides, A. & Miller, C. (1984). *J. Am. Chem. Soc.* 106, 1494–1495.
- Karipides, A., White, C. & Peiffer, K. (1992). *Acta Cryst.* C48, 1015–1018.
- Kawata, T., Uekusa, H., Ohba, S., Furukawa, T., Tokii, T., Muto, Y. & Kato, M. (1992). *Acta Cryst.* B48, 253–261.

- Kulawiec, R. J. & Crabtree, R. H. (1990). *Coord. Chem. Rev.* **99**, 89–115.
- Murray-Rust, P., Stallings, W. C., Monti, C., Preston, R. & Glusker, J. P. (1983). *J. Am. Chem. Soc.* **105**, 3206–3214.
- Rao, V. M., Sathyanarayana, D. M. & Manohar, H. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2167–2173.
- Weeks, C. M., Duax, W. L. & Wolff, M. E. (1973). *J. Am. Chem. Soc.* **95**, 2865–2868.

*Acta Cryst.* (1993). **C49**, 1923–1926

### Isostructural Mixed Ligand Complexes of $[\text{VO}]^{2+}$ and $[\text{InCl}]^{2+}$ with Hydrotris(3,5-dimethylpyrazolyl)borato and 1,3-Diphenyl-1,3-propanedionato Ligands

ROY L. BEDDOES, DAVID R. EARDLEY,  
FRANK E. MABBS,\* DAVID MOORCROFT AND  
MOHAMMAD A. PASSAND

*Department of Chemistry, University of Manchester,  
Manchester M13 9PL, England*

(Received 5 November 1992; accepted 18 May 1993)

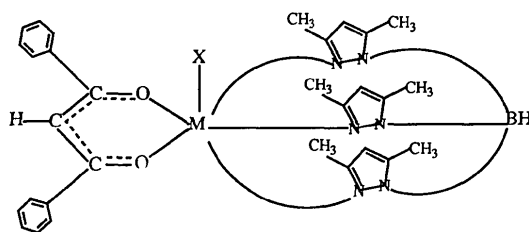
#### Abstract

The crystal and molecular structures of (1,3-diphenyl-1,3-propanedionato- $\kappa^2O,O'$ )oxo[tris(3,5-dimethyl-1-pyrazolyl- $\kappa N^2$ )hydroborato]vanadium(IV) (1) and chloro(1,3-diphenyl-1,3-propanedionato- $\kappa^2O,O'$ )[tris(3,5-dimethyl-1-pyrazolyl- $\kappa N^2$ )hydroborato]indium(III) methyl cyanide (2) have been determined. The crystals of both (1) and (2) consist of discrete six-coordinate molecules which have distorted octahedral geometries. As expected, there is a lengthening of the V—N bond *trans* to the terminal oxo group in the vanadium complex with a similar, but less pronounced, lengthening of the In—N bond *trans* to the chloro group in the indium complex.

#### Comment

We have an ongoing interest in the electron paramagnetic resonance (EPR) spectroscopy of oxovanadium(IV) species. In order to maximize the information available from single-crystal measurements it is necessary to dilute the paramagnetic compound in a diamagnetic isostructural host. We have found that in some cases compounds containing the  $[\text{MCl}]^{2+}$  moiety, where  $M = \text{Ga}$  or  $\text{In}$ , act as suitable diluents for compounds containing  $[\text{VO}]^{2+}$  (Collison, Gahan & Mabbs, 1987; Collison, Mabbs & Temperley, 1991). As part of these studies we now report the crystal structures of  $[\text{LVO}(\text{dbzac})]$  (1) and

$[\text{LInCl}(\text{dbzac})]\cdot\text{CH}_3\text{CN}$  (2), where  $L = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{hydroborato}$  and  $\text{dbzac} = 1,3\text{-diphenyl-1,3-propanedionato}$ . The structures of these two complexes are sufficiently similar for  $[\text{LInCl}(\text{dbzac})]$  to act as a suitable diamagnetic host for  $[\text{LVO}(\text{dbzac})]$ . The single-crystal EPR spectroscopy of  $[\text{LInCl}(\text{VO})(\text{dbzac})]$  will be reported elsewhere.



- (1)  $M = \text{V}$ ,  $X = \text{O}$   
(2)  $M = \text{In}$ ,  $X = \text{Cl}$

The molecular geometry in each compound is similar (Figs. 1 and 2) and consists of a distorted octahedron. As expected there is a significant lengthening of the V—N bond *trans* to the terminal oxo group [ $\text{V}(1)\text{—N}(11) = 2.326$  (5) Å compared with  $\text{V}(1)\text{—N}(21) = 2.067$  (10) and  $\text{V}(1)\text{—N}(31) = 2.121$  (10) Å]. There is a similar, but less pronounced, lengthening of the In—N bond *trans* to Cl in  $[\text{LInCl}(\text{dbzac})]$  [ $\text{In}(1)\text{—N}(11) = 2.304$  (4) Å compared with  $\text{In}(1)\text{—N}(21) = 2.213$  (4) and  $\text{In}(1)\text{—N}(31) = 2.223$  (3) Å]. The atoms within the six-membered rings comprising the metal and the  $\text{O}(41)\text{—C}(41)\text{—C}(42)\text{—C}(43)\text{—O}(42)$  part of the dbzac ligand are not coplanar. There is a significant tilting about the  $\text{O}(41)\text{—O}(42)$  direction towards the terminal monodentate ligand. The dihedral angle

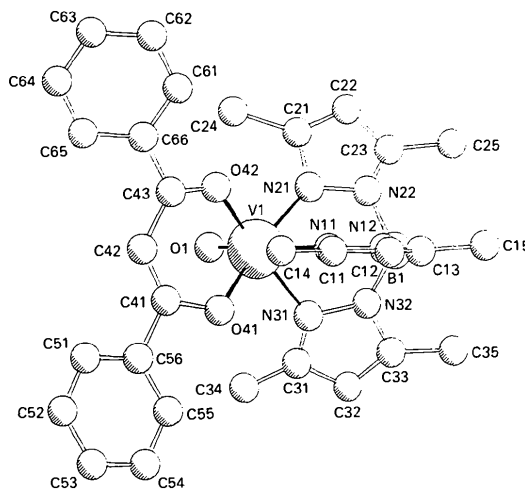


Fig. 1. PLUTO drawing (Motherwell & Clegg, 1978) of the molecular structure and the atomic numbering of  $[\text{LVO}(\text{dbzac})]$ .