

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 0.388 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.0328$	$\Delta\rho_{\min} = -0.245 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.0859$	Extinction correction:
$S = 1.060$	<i>SHELXL93</i> (Sheldrick, 1993)
2143 reflections	Extinction coefficient:
203 parameters	0.121 (8)
H atoms refined freely with isotropic displacement parameters	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.2995P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\max} = 0.009$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
Mg1	0.24658 (7)	0.35082 (6)	0.67661 (5)	0.0154 (2)
N1	0.2577 (2)	0.17876 (15)	0.86213 (12)	0.0150 (3)
C2	0.2485 (2)	0.2131 (2)	0.99113 (14)	0.0149 (3)
O2	0.2426 (2)	0.35557 (13)	1.01891 (10)	0.0192 (2)
N3	0.2443 (2)	0.0843 (2)	1.09682 (12)	0.0160 (3)
C4	0.2482 (2)	-0.0776 (2)	1.08229 (14)	0.0159 (3)
O4	0.2372 (2)	-0.18135 (13)	1.18663 (10)	0.0199 (2)
C5	0.2629 (2)	-0.1110 (2)	0.94422 (14)	0.0170 (3)
C6	0.2636 (2)	0.0187 (2)	0.84334 (14)	0.0151 (3)
C7	0.2627 (2)	-0.0032 (2)	0.69617 (14)	0.0167 (3)
O5	0.2700 (2)	-0.14467 (13)	0.66634 (11)	0.0248 (3)
O6	0.2517 (2)	0.12889 (13)	0.61315 (10)	0.0187 (2)
O7	0.2571 (2)	0.53873 (15)	0.77327 (12)	0.0243 (3)
O8	0.2454 (2)	0.4782 (2)	0.48673 (12)	0.0243 (3)
O9	-0.0885 (2)	0.44763 (14)	0.74824 (11)	0.0179 (2)
O10	0.5826 (2)	0.26320 (13)	0.59877 (11)	0.0185 (2)
O1	0.1409 (2)	0.1414 (2)	0.37733 (13)	0.0407 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mg1—O7	2.0128 (13)	C2—N3	1.385 (2)
Mg1—O8	2.0327 (13)	N3—C4	1.370 (2)
Mg1—O6	2.0393 (12)	C4—O4	1.249 (2)
Mg1—O9	2.1198 (13)	C4—C5	1.428 (2)
Mg1—O10	2.1295 (13)	C5—C6	1.358 (2)
Mg1—N1	2.1663 (14)	C6—C7	1.528 (2)
N1—C2	1.354 (2)	C7—O5	1.243 (2)
N1—C6	1.361 (2)	C7—O6	1.262 (2)
C2—O2	1.247 (2)		
O7—Mg1—O8	97.76 (6)	O2—C2—N1	122.90 (12)
O7—Mg1—O6	168.21 (5)	O2—C2—N3	118.75 (12)
O9—Mg1—O10	177.54 (4)	N1—C2—N3	118.35 (12)
O7—Mg1—N1	91.15 (5)	C4—N3—C2	125.30 (12)
O8—Mg1—N1	170.88 (5)	O4—C4—N3	119.46 (12)
O6—Mg1—N1	77.31 (5)	O4—C4—C5	125.64 (13)
O9—Mg1—N1	90.12 (6)	N3—C4—C5	114.90 (12)
O10—Mg1—N1	92.20 (6)	C6—C5—C4	118.40 (13)
C2—N1—C6	118.04 (12)	C5—C6—N1	124.96 (13)
C2—N1—Mg1	128.83 (9)		

All non-H atoms were refined anisotropically. H atoms were located from a difference Fourier map and refined isotropically.

Data collection: AFC-7S software. Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1993). Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Arrizabalaga, P., Castan, P. & Dahan, F. (1983). *Inorg. Chem.* **22**, 2245–2251.
- Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.
- Kumberger, O., Riede, J. & Schmidbaur, H. (1991). *Chem. Ber.* **124**, 2739–2742.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Mutikainen, I. (1989). *Inorg. Chim. Acta*, **36**, 155–158.
- Mutikainen, I. (1996). Unpublished results.
- Mutikainen, I. & Lumme, P. (1980). *Acta Cryst.* **B36**, 2233–2237.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sabat, M., Zgliniska, D. & Jezowska-Trzebiatowska, B. (1980). *Acta Cryst.* **B36**, 1187–1189.
- Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Victor, J., Greenberg, L. B. & Sloan, D. L. (1979). *J. Biol. Chem.* **254**, 2647–2653.

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Tetrakis(1-methylimidazole-*N*³)zinc(II) Diperchlorate

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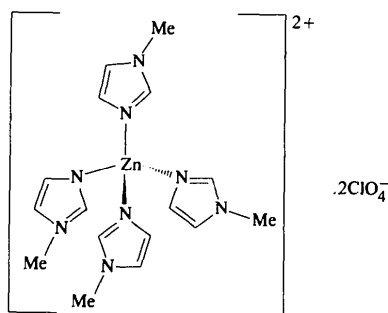
(Received 23 April 1996; accepted 10 June 1996)

Abstract

The structure of the title complex, [Zn(C₄H₆N₂)₄](ClO₄)₂, is comprised of discrete [Zn(MeIm)₄]²⁺ (MeIm is *N*-methylimidazole) cations and perchlorate anions. The Zn atom is coordinated by four MeIm ligands in a distorted tetrahedral arrangement, with a Zn—N distance of 1.991 (2) Å and N—Zn—N bond angles ranging from 103.00 (14) to 112.80 (8)°.

Comment

Metal complexes of imidazole and its derivatives are of current interest in the investigation of model complexes relevant to metalloenzymes, since imidazole, a residue of histidine, is frequently found to ligate metal ions in the active centers of metalloenzymes. Only a limited number of zinc(II) imidazole complexes have been structurally characterized (Chen, Xu & Huang, 1994; Kimura, Kurogi, Shionoya & Shira, 1991). In the course of our systematic study of metal complexes of imidazole-like ligands, we isolated the title complex, $[\text{Zn}(\text{MeIm})_4](\text{ClO}_4)_2$ (MeIm is *N*-methylimidazole), (I), and report herein its preparation and structure.



(I)

The crystal structure of (I) consists of monomeric $[\text{Zn}(\text{MeIm})_4]^{2+}$ cations and perchlorate anions. The Zn^{II} atom is located at a 4 site, being coordinated by four MeIm ligands symmetrically related by the 4 axis, resulting in a distorted tetrahedral coordination environment (Fig. 1). The Zn—N bonds are hence of an identical length [1.991 (2) Å] and the N—Zn—N bond angles range from 103.00 (14) to 112.80 (8)°. The Zn— N_{MeIm} bond lengths are comparable to the

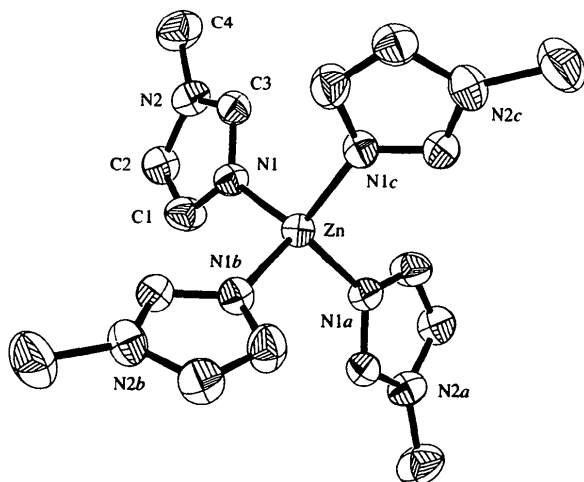


Fig. 1. ORTEP (Johnson, 1965) plot (30% probability) of the $[\text{Zn}(\text{MeIm})_4]^{2+}$ cation. H atoms and the disordered ClO_4^- anion have been omitted for clarity. [Symmetry codes: (a) $2-x, -y, z$; (b) $1+y, 1-x, -1+z$; (c) $1-y, -1+x, -1+z$.]

Zn— N_{Him} (Him is imidazole) bond lengths found in tetrahedrally-coordinated zinc(II) complexes such as $[\text{Zn}(\text{Him})_2(\text{MeCO}_2)_2]$ [1.996 (2) and 2.003 (3) Å; Chen, Xu & Huang, 1994] and $[\text{Zn}(\text{Him})_2(\text{ClO}_4)_2]$ (1.999 Å; Bear, Duggan & Freeman, 1975).

Experimental

An aqueous solution (2 ml) of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1.0 mmol) was added to an aqueous ethanolic solution (8 ml, 80%) of MeIm (0.51 g, 3.0 mmol). The mixture was heated at 333 K and stirred for 20 min. The resulting solution was allowed to stand in air whereupon colorless crystals of the title complex deposited after two weeks.

Crystal data

$[\text{Zn}(\text{C}_4\text{H}_6\text{N}_2)_4](\text{ClO}_4)_2$
 $M_r = 592.70$
 Tetragonal
 $I\bar{4}2d$
 $a = 18.616$ (3) Å
 $c = 7.4480$ (10) Å
 $V = 2581.1$ (7) Å³
 $Z = 4$
 $D_x = 1.525$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 8-13^\circ$
 $\mu = 1.214$ mm⁻¹
 $T = 293$ (2) K
 Polyhedral
 $0.36 \times 0.30 \times 0.26$ mm
 Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: semi-empirical (NRCVAX; Gabe, Le Page, Charland, Lee & White, 1989)
 $T_{\text{min}} = 0.6327$, $T_{\text{max}} = 0.9956$
 2752 measured reflections
 727 independent reflections

639 observed reflections [$I > 2\sigma(I)$]
 $R_{\text{int}} = 0.0501$
 $\theta_{\text{max}} = 25.94^\circ$
 $h = -22 \rightarrow 22$
 $k = -22 \rightarrow 22$
 $l = -9 \rightarrow 9$
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.020%

Refinement

Refinement on F^2
 $R(F) = 0.0534$
 $wR(F^2) = 0.1454$
 $S = 1.153$
 726 reflections
 98 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0999P)^2 + 0.3587P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.161$

$\Delta\rho_{\text{max}} = 0.439$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.300$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983)
 Flack parameter = 0.38 (7)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zn	1	0	-1/2	0.04588 (13)
N1	0.93166 (12)	-0.04833 (13)	-0.3336 (3)	0.0499 (6)
N2	0.88163 (14)	-0.13187 (14)	-0.1720 (4)	0.0600 (7)
C1	0.8880 (2)	-0.0170 (2)	-0.2116 (4)	0.0712 (10)

C3	0.92743 (15)	-0.1177 (2)	-0.3050 (4)	0.0548 (8)
C2	0.8559 (2)	-0.0669 (2)	-0.1117 (5)	0.0669 (9)
C4	0.8611 (2)	-0.2041 (2)	-0.1057 (8)	0.0997 (14)
Cl	3/4	-0.10848 (7)	3/8	0.0772 (4)
O1†	0.8299 (2)	-0.1163 (3)	0.3293 (8)	0.105 (2)
O2†	0.7447 (2)	-0.0404 (2)	0.4333 (8)	0.145 (3)
O3†	0.7161 (3)	-0.1317 (4)	0.2318 (7)	0.188 (4)
O4†	0.7480 (4)	-0.1570 (3)	0.5207 (6)	0.126 (2)

† Site-occupancy factor of 0.50.

Table 2. Selected geometric parameters (Å, °)

Zn—N1	1.991 (2)	N2—C2	1.376 (4)
N1—C3	1.311 (4)	N2—C4	1.483 (5)
N1—C1	1.352 (4)	C1—C2	1.332 (5)
N2—C3	1.333 (4)		
N1 ⁱ —Zn—N1 ⁱⁱ	112.80 (8)	C3—N2—C4	126.3 (3)
N1 ⁱ —Zn—N1	103.00 (14)	C2—N2—C4	126.8 (3)
C3—N1—C1	106.3 (3)	C2—C1—N1	110.1 (3)
C3—N1—Zn	125.8 (2)	N1—C3—N2	110.7 (3)
C1—N1—Zn	127.4 (2)	C1—C2—N2	106.0 (3)
C3—N2—C2	106.9 (3)		

Symmetry codes: (i) 2 - x, -y, z; (ii) 1 + y, 1 - x, -1 - z.

The O atoms of the twofold disordered perchlorate anion were subjected to geometrical restraints with site-occupancy factors of 0.50. H atoms were placed at calculated positions riding on their carrier atoms.

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bear, C. A., Duggan, K. A. & Freeman, H. C. (1975). *Acta Cryst.* **B31**, 2713–2717.
- Chen, X.-M., Xu, Z.-T. & Huang, X.-C. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2331–2332.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- 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 University Press.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Kimura, E., Kurogi, Y., Shionoya, M. & Shira, M. (1991). *Inorg. Chem.* **30**, 4524–4529.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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A Methoxycarbonyl-Substituted Cyclopentadienyl-Dicarbonyl-Trimethylphosphite-Molybdenum Complex Dimer, [Mo(η⁵-MeO₂C₂Cp){P(OMe)₃}(CO)₂]₂

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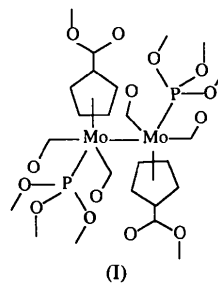
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Abstract

The title compound, bis[di(carbonyl-*C*)(η⁵-methoxycarbonylcyclopentadienyl)(trimethylphosphite-*P*)molybdenum](*Mo—Mo*), [Mo(η-C₇H₇O₂)(C₃H₉PO₃)(CO)₂]₂, belongs to a type of dinuclear molybdenum complex with an Mo—Mo single-bond length of 3.230 (4) Å. The molecule has *C*_i symmetry, with two asymmetric units which are connected through the Mo—Mo bond.

Comment

The chemistry of molybdenum-cyclopentadienyl-carbonyl complexes with metal-metal multiple bonds is of interest due to their rich reactivities. It has been found that the unsubstituted and methyl-substituted cyclopentadienyl-dicarbonylmolybdenum complexes [C₅R₅(CO)₂Mo]₂ (*R* = H or Me) differ markedly in their behaviour when reacted with trimethylphosphite, P(OMe)₃ (Curtis & Klingler, 1978; Riess, Klement & Wachter, 1985). We report here the crystal structure of the title compound, (I), which is the product of the reaction of methoxycarbonyl-substituted cyclopentadienyl-dicarbonylmolybdenum dimer and trimethylphosphite.



An *ORTEP* (Johnson, 1976) diagram of the structure of the title compound is shown in Fig. 1. The structure consists of two asymmetric units, with each asymmetric unit having the formula (MeO₂CCp)[P(OMe)₃](CO)₂Mo

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