$\theta/2\theta$ scans
Absorption correction: analytical
$T_{min} = 0.112$, $T_{max} = 0.493$
4279 measured reflections
2140 independent reflections

$R_{int} = 0.0288$
$\theta_{max} = 30.02°$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 100 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.0185$
$wR(F^2) = 0.0456$
$S = 1.009$
2140 reflections
117 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 0.0625P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.003$

$\Delta\rho_{max} = 0.987$ e Å^{-3}
$\Delta\rho_{min} = -1.162$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00042 (13)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
W(1)	0	0.632666 (9)	1/4	0.03584 (6)
C(1)	0.1416 (4)	0.5367 (2)	0.3155 (2)	0.0477 (6)
O(1)	0.2271 (4)	0.4796 (2)	0.3528 (2)	0.0715 (7)
C(2)	0.1793 (4)	0.6283 (2)	0.1380 (2)	0.0462 (6)
O(2)	0.2802 (5)	0.6216 (2)	0.0753 (2)	0.0781 (9)
N(1)	0.1453 (3)	0.7483 (2)	0.33031 (14)	0.0401 (4)
C(3)	0.0591 (4)	0.8212 (2)	0.3655 (2)	0.0494 (6)
C(4)	0.1455 (5)	0.8915 (3)	0.4159 (2)	0.0572 (7)
C(5)	0.3277 (5)	0.8875 (3)	0.4300 (2)	0.0580 (7)
C(6)	0.4186 (5)	0.8126 (3)	0.3957 (3)	0.0610 (8)
C(7)	0.3248 (4)	0.7449 (2)	0.3467 (2)	0.0507 (6)

Table 2. *Selected geometric parameters (Å, °)*

W(1)—C(1)	1.956 (3)	C(1)—O(1)	1.160 (3)
W(1)—C(2)	2.027 (3)	C(2)—O(2)	1.140 (4)
W(1)—N(1)	2.272 (2)		
C(1^i)—W(1)—C(1)	87.90 (12)	C(2)—W(1)—N(1)	93.55 (9)
C(1^i)—W(1)—C(2)	89.99 (11)	C(2^i)—W(1)—N(1)	89.19 (10)
C(1)—W(1)—C(2)	87.37 (12)	N(1)—W(1)—N(1^i)	83.33 (11)
C(2)—W(1)—C(2^i)	176.34 (15)	O(1)—C(1)—W(1)	178.8 (2)
C(1^i)—W(1)—N(1)	175.80 (9)	O(2)—C(2)—W(1)	176.9 (3)
C(1)—W(1)—N(1)	94.47 (11)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Nitrato(2,3,7,8,12,13,17,18-octaethylporphyrinato)iron(III)

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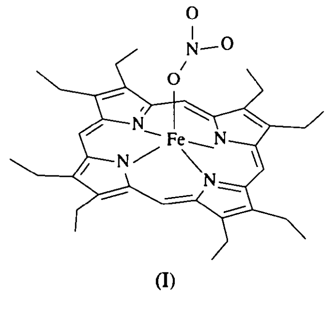
Abstract

The crystal structure of [$Fe(C_{36}H_{44}N_4)(NO_3)$] has been determined in the space group $P\bar{1}$. The unit cell contains two molecules. The Fe atom is displaced out of the porphyrin plane by 0.50 Å, the average Fe—N_p distance is 2.056 (1) Å (where N_p is a porphyrin N atom) and the Fe—O(NO_3) bond length is 2.016 (3) Å.

Comment

The isolation of the title five-coordinate iron(III)–nitrate complex, (I), resulted from attempts to isolate the six-coordinate iron(III)–nitro–nitrosyl species [Fe(OEP)(NO)(NO_2)] (where OEP is 2,3,7,8,12,13,17,18-octaethylporphyrinato; Yoshimura, 1984; Settin & Fanning, 1988).



(I)

The average Fe—N_p bond length (where N_p is a porphyrin N atom) and the Fe—O(NO_3) bond length are typical of high-spin iron(III)–porphyrin species (Scheidt & Reed, 1981) (Fig. 1). Average bond parameters and

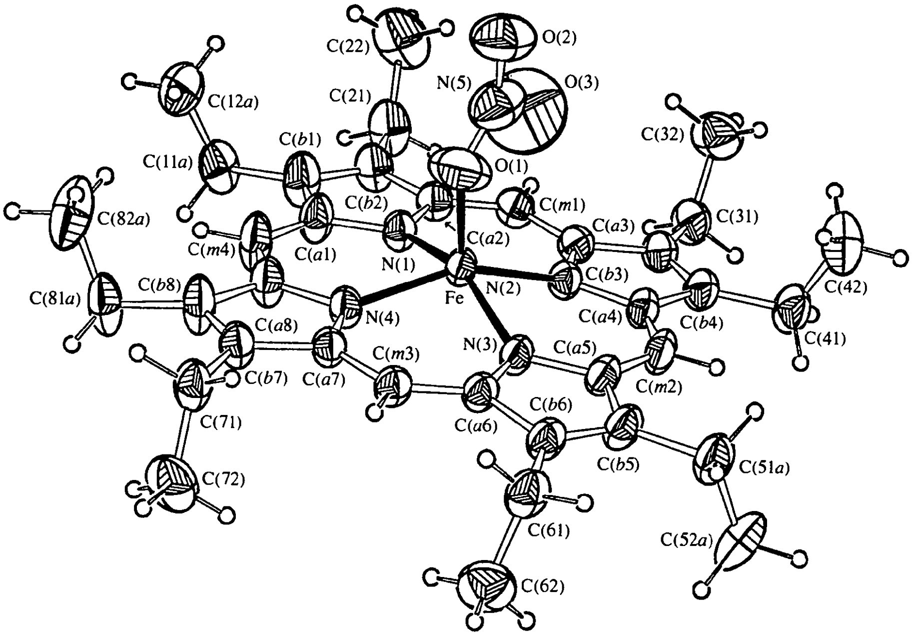


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of [Fe(OEP)(NO_3)] showing the labeling scheme. Displacement ellipsoids are drawn at the 40% probability level.

atom displacements from the mean 24-atom porphyrin plane are shown in Fig. 2. The IR spectrum of a nujol mull of [Fe(OEP)(NO_3)] exhibits a band at 1515 cm^{-1}, which is indicative of a bound nitrate. The nitrate is coordinated through a single O atom, which is in distinct contrast to that in [Fe(TPP)(NO_3)] (Phillippi, Baenziger & Goff, 1981), where the nitrate is bound in an unsymmetrical bidentate mode. The Fe atom is in the plane of the nitrate anion in both structures. The bidentate nitrate is oriented between two pyrrole N atoms. The monodentate nitrate makes a dihedral angle of 31° with the plane defined by the Fe, N(4) and O(1) atoms. This difference is probably a result of the greater steric demands of bidentate coordination. The steric requirements are also reflected in the average Fe—N_p bond distances {Fe—N_p 2.073 (12) in [Fe(TPP)(NO_3)] and 2.056 (1) Å in [Fe(OEP)(NO_3)]}, as well as in the Fe-atom displacement out of the 24-atom porphyrin core {0.60 in [Fe(TPP)(NO_3)] and 0.50 Å in [Fe(OEP)(NO_3)]}.

Three of the eight ethyl groups are disordered on two sets of positions [C(11*a*) and C(12*a*) *versus* C(11*b*) and C(12*b*), C(51*a*) and C(52*a*) *versus* C(51*b*) and C(52*b*), and C(81*a*) and C(82*a*) *versus* C(81*b*) and C(82*b*)]. The group-occupancy coefficients of the three ethyl groups on their two sets of positions converged to 0.78:0.22, 0.89:0.11 and 0.62:0.38, respectively. The C—C bond lengths of these ethyl groups were restrained to a target value of 1.513 Å, with a standard deviation of 0.003. The C—C bond lengths of the pyrrole C atoms and the ethyl groups were restrained to a value of 1.510 Å, with a standard deviation of 0.003.

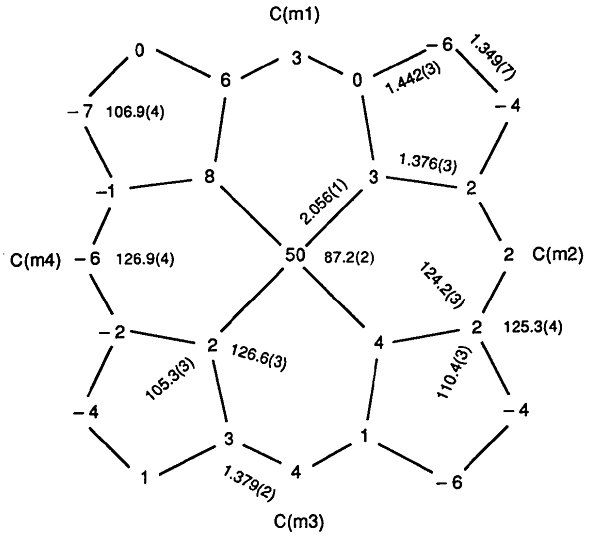


Fig. 2. Formal diagram of the 24-atom porphyrinato core of [Fe(OEP)(NO_3)]. The perpendicular displacements (in units of 0.01 Å) from the 24-atom mean plane of the porphyrin core are shown. Also shown are the average values for the bond parameters.

Experimental

Nitric oxide gas was bubbled into a solution of [Fe(OEP)$_2$O] in chloroform. Crystals of the iron nitrate complex were obtained by liquid diffusion using hexanes as the non-solvent. No attempt was made to exclude oxygen.

Crystal data

[Fe($C_{36}H_{44}N_4$)(NO_3)]
M_r = 650.61

Mo *Kα* radiation
λ = 0.71073 Å

Triclinic
$P\bar{1}$
$a = 10.4304(3)$ Å
$b = 10.8912(9)$ Å
$c = 15.8159(15)$ Å
$\alpha = 72.231(7)°$
$\beta = 72.719(11)°$
$\gamma = 82.798(7)°$
$V = 1632.5(2)$ Å^3
$Z = 2$
$D_x = 1.324$ Mg m^{-3}
D_m not measured

Cell parameters from 250 reflections
$\theta = -20.5$–$20.5°$
$\mu = 0.506$ mm^{-1}
$T = 293(2)$ K
Block-shaped
$0.20 \times 0.16 \times 0.10$ mm
Black

Data collection

Enraf–Nonius FAST area-detector diffractometer
Ellipsoid-mask fitting scans
Absorption correction: none
15 949 measured reflections
7949 independent reflections
5554 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.049$
$\theta_{\rm max} = 29.86°$
$h = -13 \rightarrow 10$
$k = -15 \rightarrow 13$
$l = -22 \rightarrow 22$
Intensity decay: no measurable crystal decay

Refinement

Refinement on F^2
$R(F) = 0.060$
$wR(F^2) = 0.134$
$S = 1.071$
7949 reflections
463 parameters
H atoms: idealized with riding model, aromatic C—H = 0.93 Å, aliphatic C—H = 0.96–0.97 Å

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 1.3666P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.010$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.48$ 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)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe	0.58512 (4)	0.49231 (4)	0.73749 (3)	0.03847 (13)
N(1)	0.7104 (2)	0.3808 (2)	0.8123 (2)	0.0439 (6)
N(2)	0.5296 (2)	0.5941 (2)	0.8338 (2)	0.0438 (6)
N(3)	0.4034 (2)	0.5520 (2)	0.7098 (2)	0.0413 (5)
N(4)	0.5795 (2)	0.3361 (2)	0.6916 (2)	0.0424 (5)
C(*a*1)	0.7812 (3)	0.2699 (3)	0.7996 (3)	0.0578 (9)
C(*a*2)	0.7590 (3)	0.4147 (3)	0.8738 (2)	0.0451 (7)
C(*a*3)	0.6004 (3)	0.5985 (3)	0.8937 (2)	0.0450 (7)
C(*a*4)	0.4352 (3)	0.6939 (3)	0.8357 (2)	0.0470 (7)
C(*a*5)	0.3243 (3)	0.6572 (3)	0.7280 (2)	0.0470 (7)
C(*a*6)	0.3518 (3)	0.5158 (3)	0.6507 (2)	0.0420 (6)
C(*a*7)	0.5079 (3)	0.3298 (3)	0.6327 (2)	0.0410 (6)
C(*a*8)	0.6700 (3)	0.2329 (3)	0.6926 (3)	0.0575 (9)
C(*b*1)	0.8770 (4)	0.2340 (3)	0.8536 (3)	0.0688 (11)
C(*b*2)	0.8648 (4)	0.3248 (3)	0.8974 (2)	0.0569 (9)
C(*b*3)	0.5470 (3)	0.7019 (3)	0.9351 (2)	0.0511 (7)
C(*b*4)	0.4461 (3)	0.7612 (3)	0.8990 (2)	0.0522 (8)
C(*b*5)	0.2213 (3)	0.6855 (3)	0.6800 (2)	0.0526 (8)
C(*b*6)	0.2371 (3)	0.5979 (3)	0.6330 (2)	0.0471 (7)
C(*b*7)	0.5553 (3)	0.2221 (3)	0.5957 (2)	0.0498 (7)
C(*b*8)	0.6552 (4)	0.1607 (3)	0.6337 (3)	0.0705 (11)
C(*m*1)	0.7072 (3)	0.5160 (3)	0.9107 (2)	0.0477 (7)
C(*m*2)	0.3417 (3)	0.7223 (3)	0.7859 (2)	0.0538 (8)
C(*m*3)	0.4028 (3)	0.4145 (3)	0.6137 (2)	0.0432 (6)
C(*m*4)	0.7614 (4)	0.2023 (4)	0.7442 (3)	0.0726 (12)
C(11*a*)†	0.9595 (5)	0.1083 (4)	0.8664 (4)	0.065 (2)
C(12*a*)†	1.0822 (5)	0.1210 (6)	0.7847 (4)	0.089 (2)
C(11*b*)†	1.0084 (9)	0.1665 (13)	0.8168 (10)	0.060 (7)
C(12*b*)†	0.983 (2)	0.0280 (15)	0.8738 (16)	0.097 (8)
C(21)	0.9469 (4)	0.3331 (4)	0.9591 (3)	0.0738 (12)
C(22)	1.0703 (5)	0.4098 (5)	0.9068 (4)	0.105 (2)
C(31)	0.5977 (4)	0.7336 (4)	1.0055 (3)	0.0624 (9)
C(32)	0.7093 (4)	0.8256 (5)	0.9618 (3)	0.0837 (13)
C(41)	0.3616 (4)	0.8784 (4)	0.9163 (3)	0.0658 (10)
C(42)	0.4149 (5)	1.0020 (4)	0.8467 (3)	0.0912 (14)
C(51*a*)†	0.1205 (4)	0.7977 (4)	0.6820 (3)	0.0607 (15)
C(52*a*)†	0.0039 (4)	0.7703 (5)	0.7682 (3)	0.080 (2)
C(51*b*)†	0.0855 (11)	0.747 (2)	0.716 (3)	0.043 (11)
C(52*b*)†	0.113 (4)	0.889 (3)	0.676 (3)	0.083 (14)
C(61)	0.1541 (3)	0.5808 (3)	0.5750 (2)	0.0576 (9)
C(62)	0.0580 (4)	0.4721 (4)	0.6251 (3)	0.0800 (12)
C(71)	0.4986 (3)	0.1853 (3)	0.5304 (2)	0.0559 (8)
C(72)	0.3804 (4)	0.1013 (4)	0.5793 (3)	0.0795 (12)
C(81*a*)†	0.7162 (8)	0.0260 (5)	0.6373 (7)	0.073 (3)
C(82*a*)†	0.8595 (9)	0.0401 (8)	0.5773 (5)	0.104 (3)
C(81*b*)†	0.7603 (10)	0.0705 (9)	0.5922 (7)	0.061 (4)
C(82*b*)†	0.7295 (13)	−0.0593 (11)	0.6629 (8)	0.092 (5)
O(1)	0.6939 (3)	0.5839 (3)	0.6095 (3)	0.0996 (11)
N(5)	0.7707 (4)	0.6609 (4)	0.6054 (3)	0.0850 (11)
O(2)	0.8433 (3)	0.7231 (3)	0.5351 (2)	0.0973 (10)
O(3)	0.7721 (6)	0.6648 (6)	0.6806 (3)	0.189 (3)

† Site-occupancy factors: C(11*a*) and C(12*a*) 0.779 (10), C(11*b*) and C(12*b*) 0.221 (10), C(51*a*) and C(52*a*) 0.891 (9), C(51*b*) and C(52*b*) 0.109 (9), C(81*a*) and C(82*a*) 0.615 (10), and C(81*b*) and C(82*b*) 0.385 (10).

Table 2. *Selected geometric parameters (Å, °)*

Fe—O(1)	2.016 (3)	Fe—N(4)	2.056 (2)
Fe—N(1)	2.056 (2)	O(1)—N(5)	1.206 (5)
Fe—N(2)	2.056 (2)	O(2)—N(5)	1.198 (4)
Fe—N(3)	2.054 (2)	O(3)—N(5)	1.208 (6)
N(1)—Fe—O(1)	109.86 (12)	N(2)—Fe—N(3)	87.13 (9)
N(2)—Fe—O(1)	117.40 (13)	N(2)—Fe—N(4)	153.35 (10)
N(3)—Fe—O(1)	94.20 (12)	N(3)—Fe—N(4)	86.99 (9)
N(4)—Fe—O(1)	88.95 (13)	N(5)—O(1)—Fe	115.8 (3)
N(1)—Fe—N(2)	87.39 (9)	O(2)—N(5)—O(3)	112.8 (5)
N(1)—Fe—N(3)	155.08 (10)	O(2)—N(5)—O(1)	124.5 (5)
N(1)—Fe—N(4)	87.09 (9)	O(3)—N(5)—O(1)	112.7 (5)

Our detailed methods and procedures for small molecule X-ray data collection with the Enraf–Nonius FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). The structure was solved in the space group $P1$ by the direct methods program *SHELXS*86 (Sheldrick, 1990). All non-H atoms were located on an E map, except for several ethyl C atoms, which were found in succeeding difference Fourier syntheses. The positional parameters were then deduced for the corresponding $P\bar{1}$ group and refined anisotropically with *SHELXL*93 (Sheldrick, 1993).

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1259). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cadmium(II) Complex of Creatinine, $[Cd(C_2H_3O_2)_2(C_4H_7N_3O)_2].0.5H_2O$

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(*Received 30 April 1996; accepted 22 July 1996*)

Abstract

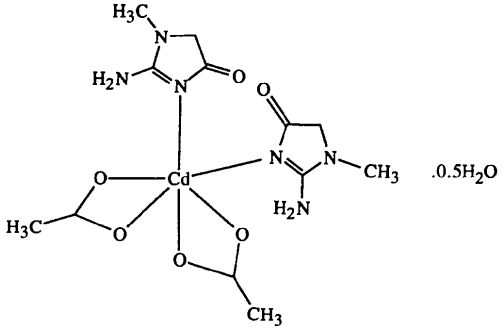
The crystal structure of bis(acetato-*O*,*O*′)bis(2-amino-1,5-dihydro-1-methyl-4*H*-imidazol-4-one-N^3)cadmium(II) hemihydrate, $[Cd(CH_3CO_2)_2(creat)_2].0.5H_2O$, shows the coordination geometry around the Cd atom to be distorted octahedral involving two monodentate heterocyclic N-bound creatinine molecules and two *O*,*O*-bidentate acetate groups.

Comment

Creatinine is the final catabolic product of creatine. The concentration of creatinine in blood and urine is an important factor in assessing renal function. In order to probe the metabolic processes that occur with creatinine, many studies investigating the coordination chemistry of the ligand have been carried out and, more recently, comprehensively reviewed (Mitewa, 1995).

Structural studies involving creatinine include its phenylmercury(II) (Canty, Fyfe & Gatehouse, 1978; Canty, Chaichit & Gatehouse, 1979), silver(I) (Udupa & Krebs, 1981), tetrachlorocuprate(II) (Udupa & Krebs, 1979), platinum(II) (Mitewa, Gencheva, Bontchev, Angelova & Maciček, 1988; Maciček, Angelova, Gencheva, Mitewa & Bontchev, 1988; Beurskens, Perales, Martin-Gil & Martin-Gil, 1988; Beja, Paixao, Martin-Gil & Salgado, 1991; Gencheva *et al.*, 1992) and palladium(II) (Beurskens *et al.*, 1988) complexes.

As part of our studies (Chotalia, Hambley, Ridley & Turner, 1996) on the modes of coordination of creatinine with different metal ions, we have investigated the reactivity of the ligand with the Group 12 metal triad. At the time of the preparation of this communication, the structures of $[Zn(creat)_2Cl_2]$ (Okabe, Kohyama & Ikeda, 1995) and $[Cd(creat)_2Cl_2]$ (Okabe, Ikeda & Kohyama, 1995) had been reported. Both have four-coordinate tetrahedral metal centres coordinated by two imidazole N atoms and two Cl atoms. The title compound, $[Cd(creat)_2(CH_3CO_2)_2].0.5H_2O$, (I), was obtained upon mixing creatinine and $[Cd(CH_3CO_2)_2].2H_2O$ in ethanol–acetone (1:1).



(I)

The structure of (I) with the atom numbering is shown in Fig. 1. The metal ion is in a distorted octahedral environment, coordinated by two creatinine imidazole

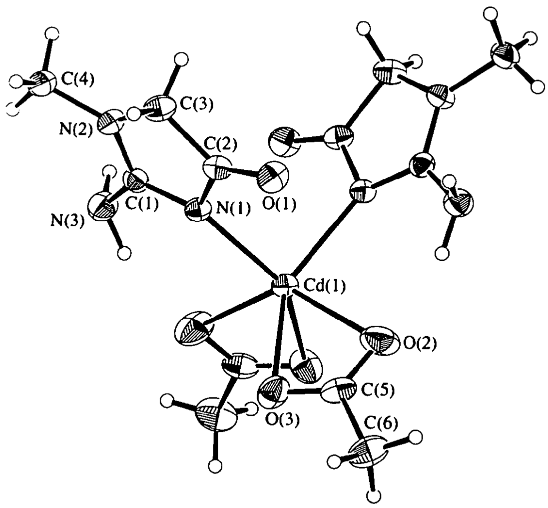


Fig. 1. A perspective view showing the structure of $[Cd(creat)_2(CH_3CO_2)_2]$ and the atom-numbering scheme. Displacement ellipsoids are shown at the 25% probability level.

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