Synthesis, characterization, and crystal and molecular structures of caesium *N*-(carbamoylethyl)iminodiacetatooxoperoxovanadate(V) monohydrate

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A new monoperoxo complex of vanadium(V) of composition $Cs[VO(O_2)(CEIDA)] \cdot H_2O$ [where H_2CEIDA is *N*-(carbamoylethyl)iminodiacetic acid] was prepared and characterized by IR, UV-VIS and ^{51}V NMR spectroscopies. Thermal analysis showed that after crystal water release the anhydrous $Cs[VO(O_2)(CEIDA)]$ is formed, which is stable over a relatively large temperature interval and can be isolated by interruption of the dynamic heating in that interval. The X-ray structure analysis of $Cs[VO(O_2)(CEIDA)] \cdot H_2O$ revealed a mononuclear structure of the complex anion with a typical distorted pentagonal bipyramidal arrangement around vanadium formed by two peroxo oxygens bound in an η^2-fashion, two oxygens from the deprotonated carboxylic groups and a nitrogen in the equatorial plane, and an oxo ligand and an oxygen from the carbamoyl group in the apical positions. The heteroligand is thus bound as a tetradentate CEIDA(2−)-*N,O,O,O* ligand to form one six-membered and two glycinate rings.

Determination of the crystal structures of the native and peroxide forms of the vanadium-containing chloroperoxidase from *Curvularia inaequalis* fungus showed that vanadium atom in the active site of the enzyme is coordinated by four non-protein oxygens and one nitrogen atom from a histidine.[1,2] The peroxide form can thus be regarded as a monoperoxo complex with the peroxo ligand coordinated in an η^2-fashion, which is the same as found in structures of all mono- and dinuclear vanadium(V) monoperoxo complexes. The study of such complexes with heteroligands containing one nitrogen and several oxygen atoms completing the coordination sphere of vanadium is important, as these complexes provide useful models for intermediates formed on interaction of the vanadium haloperoxidase with hydrogen peroxide. To date, the monoperoxo complexes of vanadium(V) with nitrilotriacetate(3−) (NTA),[3–8] hydroxyethyliminodiacetate(2−) (HHEIDA)[9] and *N*-(carbamoylmethyl)iminodiacetate(2−) (ADA)[9,10] as tetradentate ligands, all containing an O_3N donor set, have been prepared and structurally characterized. We report here the preparation, thermal and spectral properties and the crystal and molecular structures of $Cs[VO(O_2)(CEIDA)] \cdot H_2O$, where CEIDA is *N*-(carbamoylethyl)iminodiacetate(2−). The study of $[VO(O_2)(CEIDA)]^-$ ion formation in aqueous solution (pH 1–4) has been reported earlier by one of us.[11]

Experimental

Chemicals and apparatus

V_2O_5 was prepared by thermal decomposition of NH_4VO_3 (Loba Chemie). H_2CEIDA was synthesized from 3-chloropropionamide and iminodiacetic acid (Aldrich) as described in the literature.[12] All other chemicals were supplied by Lachema.

Vanadium content was determined by titration with $FeSO_4$ (diphenylamine as indicator) in a sample that was previously annealed in a Pt crucible. C, H and N were determined on a Carlo Erba 1106 analyzer. Caesium was estimated on a isotachophoretic analyzer ZTKI 01 (URVST Slovakia).

The IR spectra were measured on a Nicolet Magna 750 FT IR spectrophotometer, the UV-VIS spectra on a Hewlett Packard 8452 spectrometer and ^{51}V NMR spectrum on a Bruker DRX 500 spectrometer with $VOCl_3$ as external standard. The thermal analysis was performed on a Q-1500 Derivatograph (MOM, Budapest) with the following conditions: sample weight, 100 mg; heating rate, 0.6 °C min^{-1}; air atmosphere.

Syntheses

Synthesis of $Cs[VO(O_2)(CEIDA)] \cdot H_2O$ (1). V_2O_5 (0.091 g, 5 mmol) was dissolved in 2 ml of 30% H_2O_2. The solution formed was diluted by 20 ml H_2O. Solid CsCl (0.168 g, 1 mmol) and H_2CEIDA (0.204 g, 1 mmol) were then slowly dissolved in the diluted peroxovanadium(V) solution. The crystallization was initiated by dropwise addition of 96% ethanol to the orange-red solution (pH 2.1) until formation of a stable weak turbidity. The microcrystalline orange product, which formed within 2 days, was washed with ethanol and dried at room temperature. The monocrystals for X-ray analysis were obtained by recrystallization from a water–ethanol solution at pH 2.4. Anal. calcd (%) for $CsVC_7H_{12}N_2O_9$: Cs 29.40, V 11.27, C 18.60, H 2.68, N 6.20; found: Cs 29.20, V 10.94, C 18.64, H 2.58, N 6.11. ^{51}V NMR (5×10^{-3} mol dm^{-3} in H_2O): −583.3 ppm. UV-VIS (H_2O): LMCT ($L = O_2^{2-}$) band at 438 nm, $\varepsilon = 390$ mol^{-1} dm^3 cm^{-1}. IR (Nujol, cm^{-1}): 415vw, 450w, 470m, 495w, 534w, 564s [$\nu(V{-}O_p)$], 621s, 670m, 698s, 734m, 800vw, 830m, 916vs [$\nu(O_p{-}O_p)$], 958vs [$\nu(V{=}O)$], 1026m, 1055vw, 1095sh, 1110m [$\nu(C{-}N_{coord})$], 1206m, 1238w, 1265m, 1298s, 1325vs, 1375vs, 1415s, 1600–

Table 1 Crystal data and structure refinement for $Cs[VO(O_2)(CEIDA)] \cdot H_2O$

Empirical formula	$C_7H_{12}CsN_2O_9V$
Formula weight	452.04
T/K	150.0(2)
λ/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	6.121(4)
b/Å	8.959(2)
c/Å	23.532(12)
α/°	90
β/°	96.28(5)
γ/°	90
U/Å^3	1282.7(11)
Z	4
D_c/g cm^{-3}	2.341
μ/mm^{-1}	3.617
F(000)	872
Crystal size/mm	0.70 × 0.20 × 0.10
θ range for data collection/°	1.74–25.08
Index ranges	$-7 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 10$, $-7 \leqslant l \leqslant 27$
Reflections collected	2481
Independent reflections	2238 ($R_{int} = 0.0536$)
Observed reflections ($I > 2\sigma_I$)	1960
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2238/0/211
Goodness-of-fit on F^2	1.020
Final R indices ($I > 2\sigma_I$)^a	$R_1 = 0.0476$, $R_{w2} = 0.1273$
R indices (all data)^a	$R_1 = 0.0553$, $R_{w2} = 0.1355$
Largest diff. peak and hole/e Å^{-3}	1.396 and -1.694

$^a R_1 = \Sigma \| F_o | - | F_c \| / | F_o |$; $R_{w2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

1665 vs, br [$\nu(C{=}O)_{carbamoyl}$, ν_{as}(COO), $\delta(NH_2)$, $\delta(H_2O)$] (O_p is peroxo oxygen).

Preparation of $Cs[VO(O_2)(CEIDA)]$ (2). **2** was prepared by interruption of dynamic heating during the thermal analysis of **1** at 105 °C. It was identified by CHN analysis and its IR spectrum, which still exhibits all characteristic bands of the monoperoxo complex.

Anal. calcd (%) for $CsVC_7H_{10}N_2O_8$: C 19.37, H 2.32, N 6.45; found: C 18.97, H 2.43, N 6.22. IR (Nujol, cm^{-1}): 455w, 483w, 525m, 550s, 570s [$\nu(V{-}O_p)$], 624s, 684w, 735m, 820m, 838m, 924vs [$\nu(O_p{-}O_p)$], 950vs [$\nu(V{=}O)$], 1026m, 1062w, 1094w, 1126m [$\nu(C{-}N_{coord})$], 1200m, 1239m, 1280s, 1307s, 1333s, 1405m, 1630vs, 1653vs [$\nu(C{=}O)_{carbamoyl}$, ν_{as}(COO), $\delta(NH_2)$].

X-Ray structure determination

Low-temperature X-ray measurements of **1** were made on a KUMA KM4 diffractometer with graphite monochromated Mo-K$_\alpha$ radiation using the ω–2θ scan technique. No significant decay of the intensity of three standard reflections recorded after every 90 reflections was observed. The data were not corrected for absorption effects. 2238 unique reflections were obtained, of which 1960 with $I > 2\sigma_I$ were classified as observed. Additional crystal data and refinement results are given in Table 1.

The structure was solved by a combination of Patterson and difference Fourier methods, and refined by a full-matrix least-squares procedure (SHELXL-93) on $|F^2|$.[13] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the CH_2 and NH_2 groups were obtained from a difference Fourier map and were refined isotropically with U_{eq} equaled to 1.2 × U_{eq} of the atom to which they are bonded. Two hydrogen atoms from the water molecule were not identified. The final refinement was carried out with the weighting scheme $w = 1/[(\sigma^2(F_o^2) + (0.0950P)^2 + 6.4342P]$ where $P = (F_o^2 + 2F_c^2)/3$, and with 2238 independent reflections. The refinement converged at $R_1(F) = 0.0476$ and $R_{w2}(F^2) = 0.1273$ for the observed reflections and 211 refined parameters. The largest positive and negative peaks in the difference map were 1.40 and -1.69 e Å^{-3}, respectively. CCDC reference number 440/076.

Results and discussion

The IR spectra of **1** and **2** exhibit in the expected regions all characteristic V=O, V—O$_p$ and O$_p$—O$_p$ stretches, which allow the compounds to be identified as monoperoxo complexes.[3–5,14–17] The IR spectra indicate that the CEIDA ligand is bound in both complexes *via* the imino nitrogen [shift of the band corresponding to the ν(C—N) vibration from 1193 cm^{-1} in the uncoordinated ligand to 1110 cm^{-1} in **1** and 1126 cm^{-1} in **2**] and *via* both deprotonated carboxylate groups [absence of the ν(COOH) vibration observed in H_2CEIDA at 1705 cm^{-1}]. Involvement of the carbamoyl group in the coordination with vanadium in **1**, due to the complexity of the spectrum in the 1600–1665 cm^{-1} region, could not be identified by IR.

The thermal analysis of **1** was performed under the given conditions in the temperature interval 20–180 °C. The weight loss, 3.9%, corresponding to the endothermic process in the interval 50–73 °C agrees with the calculated value, 3.98%, for loss of one water molecule. In the interval 75–155 °C no weight loss was observed; the decomposition product, obviously the anhydrous monoperoxo complex **2**, is stable in this temperature interval. A further sudden exothermic decomposition process occurred at 155 °C. The weight loss corresponding to this process, 29%, exceeds the calculated value, 7.08%, for active oxygen release. The oxygen release thus proceeds simultaneously with decomposition of the CEIDA ligand.

The crystal structure of **1** is built up of $[VO(O_2)(CEIDA)]^-$ anions, Cs$^+$ cations and water molecules held together mainly by electrostatic forces and hydrogen bonds. Their arrangement in the unit cell is shown in Fig. 1. The structure of the complex anion is shown in Fig. 2 and selected interatomic distances and angles are given in Table 2. The vanadium atom is seven-coordinated. The coordination polyhedron of vanadium is a distorted pentagonal bipyramid with carboxylic oxygens O(1), O(3), peroxo oxygens O(7), O(8) and imino

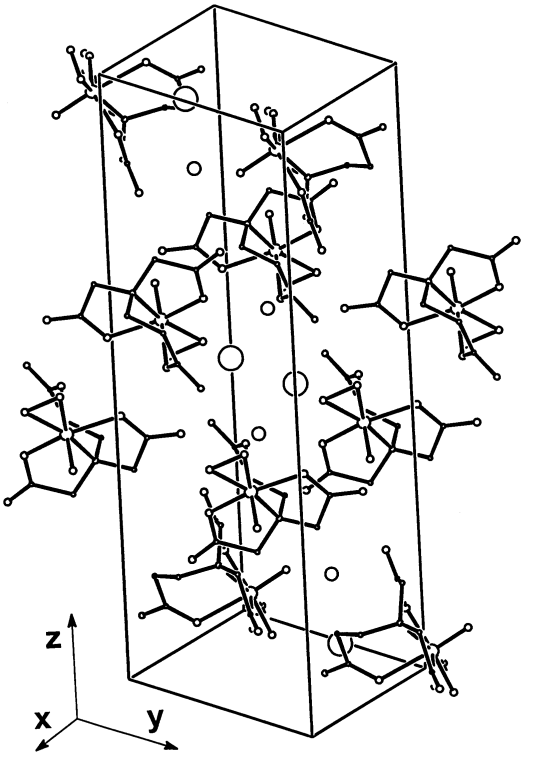

Fig. 1 Arrangement of the unit cell in the structure of $Cs[VO(O_2)(CEIDA)] \cdot H_2O$.

Table 2 Selected interatomic distances (Å) and bond angles (°) for Cs[VO(O_2)(CEIDA)$\cdot$$H_2O$

V—O(1)	2.041(4)	O(1)—C(2)	1.279(8)	Cs···O(5)^{ii}	3.106(5)
V—O(3)	2.038(5)	O(3)—C(4)	1.301(8)	Cs···O(9)w	3.205(6)
V—O(5)	2.231(5)	O(5)—C(7)	1.264(8)	Cs···O(3)^{ii}	3.248(4)
V—O(6)	1.594(4)	N(1)—C(1)	1.479(8)	Cs···O(3)^{i}	3.259(4)
V—O(7)	1.881(5)	N(1)—C(3)	1.490(8)	Cs···O(4)^{iii}	3.276(5)
V—O(8)	1.870(5)	N(1)—C(5)	1.503(8)	Cs···O(7)	3.279(5)
V—N(1)	2.165(5)	Cs···O(7)^{i}	3.089(5)	Cs···O(6)^{i}	3.340(4)
O(8)—O(7)	1.439(7)	Cs···O(8)	3.103(5)	Cs···O(7)^{ii}	3.450(6)
O(1)—V—O(3)	149.7(2)	O(5)—V—O(7)	83.6(2)	O(8)—V—N(1)	153.8(2)
O(1)—V—O(5)	82.7(2)	O(5)—V—O(8)	83.6(2)	O(7)—O(8)—V	67.9(3)
O(1)—V—O(6)	95.7(2)	O(6)—V—O(7)	102.6(2)	O(8)—O(7)—V	67.0(3)
O(1)—V—O(7)	124.4(2)	O(6)—V—O(8)	102.5(2)	C(2)—O(1)—V	118.3(4)
O(1)—V—O(8)	79.9(2)	O(7)—V—O(8)	45.1(2)	C(4)—O(3)—V	117.4(4)
O(3)—V—O(5)	83.7(2)	O(1)—V—N(1)	75.7(2)	C(7)—O(5)—V	123.6(4)
O(3)—V—O(6)	94.7(2)	O(3)—V—N(1)	76.1(2)	C(1)—N(1)—V	104.7(4)
O(3)—V—O(7)	80.5(2)	O(5)—V—N(1)	84.1(2)	C(3)—N(1)—V	105.5(4)
O(3)—V—O(8)	125.2(2)	O(6)—V—N(1)	89.3(2)	C(5)—N(1)—V	117.1(4)
O(5)—V—O(6)	173.4(2)	O(7)—V—N(1)	154.5(2)		

Symmetry transformations used to generate equivalent atoms: ^{i} $-x, -y+1, -z$; ^{ii} $x+1, y, z$; ^{iii} $-x-1, -y+1, -z$; w represents oxygen from water molecule.

nitrogen N(1) in the equatorial plane, and with the carbamoyl group oxygen O(5) and doubly bonded oxygen O(6) in the apical positions.

The five atoms in the equatorial plane are nearly coplanar, the maximum deviation from the plane is 0.016(3) Å. The vanadium atom is displaced from this plane by 0.226(2) Å towards the terminal oxygen O(6). The vanadium–apical oxygen O(5) bond length, generally elongated due to the structural *trans* influence,[18] is 2.231(5) Å in the six-membered chelate in **1**; this value is not significantly longer than in NTA, ADA and HHEIDA monoperoxo complexes with five-membered chelates (2.108–2.218 Å). The distorted pentagonal bipyramid is almost symmetric: the O(5), V, N(1), O(6) plane passes nearly through the midpoint between the O(8) and O(7) peroxo oxygens [deviations of 0.730(7) and −0.709(7) Å], and also the carboxylic oxygen atoms O(1) and O(3) are symmetrically placed with respect to this plane [deviations of 1.967(5) and −1.970(5) Å]. The symmetry of the anion with respect to this plane is disturbed by the carbon atoms C(6) and C(7) of the six-membered ring, which deviate from this plane by 1.015(9) and 0.773(8) Å, respectively. The O(7)—O(8) distance found, 1.439(7) Å, is identical with the average value found for this bond length in eight monoperoxo complexes containing a heteroligand with an O_3N donor set.[4–10] The V(O_p—O_p) group is nearly symmetric, the difference in the two V—O_p distances is 0.011 Å. The most significant difference in the structure of **1** when compared with the structures of NTA, ADA and HHEIDA complexes containig a five-membered apical chelate is the enlargement of the O(6)—V—O(5) angle from 165.87–167.7° for NTA, ADA and HHEIDA monoperoxo complexes[4–8] to 173.4(2)° in **1** (Table 2).

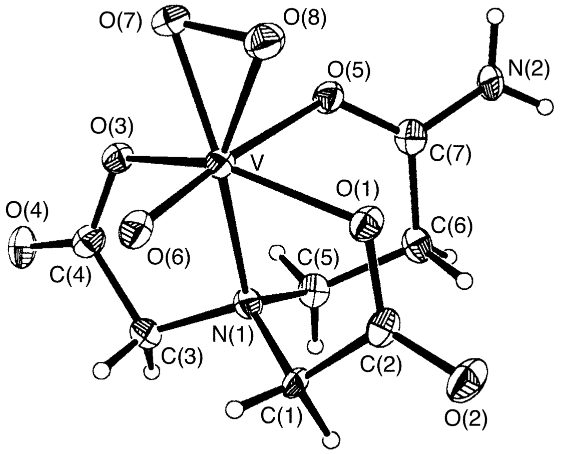

Fig. 2 ORTEP plot of the [VO(O_2)(CEIDA)]$^-$ anion at 50% probability level for non-hydrogen atoms.

Within a distance of approximately 3.50 Å, which corresponds to the highest coordination number (12) of caesium surrounded by oxygens,[19] the Cs^+ cation is in close contact with nine peroxo and carboxylic oxygen atoms belonging to four anions in different equivalent positions, and the O(9)w oxygen from the water molecule (Table 2).

The data on crystal structures with coordinated CEIDA ligand are very scarce—only three structures of Co^{III}, Cu^{II} and Ni^{II} complexes have been determined so far.[12,20,21] The structures of **1**, Cu^{II} and Ni^{II} complexes indicate an oxophilic nature of these central ions: the carbamoyl group is preferably coordinated *via* oxygen and not the nitrogen atom. In the Co^{III} complex, CEIDA is coordinated as a tridentate ligand *via* two carboxylic oxygens and imino nitrogen.

The characterized Cs[VO(O_2)(CEIDA)]$\cdot$$H_2O$ complex is the fourth complex of vanadium(v) with a heteroligand containing an O_3N donor set and the first one with a ligand forming two five- and one six-membered chelates. The thermal stability study showed that the heteroligands discussed stabilize the VO(O_2) group: oxygen release occurs at temperatures above 150 °C. The maintaining of the complex anion structure on dissolution, proved by a single chemical shift in the ^{51}V NMR spectrum, provide a possibility for using this complex in a study of oxidation ability in the reaction with halides, that is, as functional model for haloperoxidase, or in oxygen transfer reactions.

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References

1 A. Messerschmidt and R. Wever, *Proc. Natl. Acad. Sci.*, 1996, **93**, 392.
2 A. Messerschmidt, L. Prade and R. Wever, *Biol. Chem.*, 1997, **378**, 309.
3 M. Sivák, D. Joniaková and P. Schwendt, *Transition Met. Chem.*, 1993, **18**, 304.

4 C. Djordjevic, P. L. Wilkins, E. Sinn and R. J. Butcher, *Inorg. Chim. Acta*, 1995, **230**, 241.

5 L'. Kuchta, M. Sivák and F. Pavelčík, *J. Chem. Res.*, 1993, (*S*) 393, (*M*) 2801.

6 A. E. Lapshin, Y. I. Smolin, Y. F. Shepelev, M. Sivák and D. Gyepesová, *Acta Crystallogr., Sect. C*, 1993, **49**, 867.

7 Y. G. Wei, G. Q. Huang and M. C. Shao, *Polyhedron*, 1994, **13**, 1587.

8 W. Da-Xu, L. Xiu-Lian, C. Rong and M. Mao-Chun, *Liegou Huaxue* (*J. Struct. Chem.*), 1992, **11**, 65.

9 G. J. Colpas, B. J. Hamstra, J. W. Kampf and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1996, **118**, 3469.

10 M. Sivák, J. Tyršelová, F. Pavelčík and J. Marek, *Polyhedron*, 1996, **15**, 1057.

11 M. Sivák and P. Schwendt, *Transition Met. Chem.*, 1989, **14**, 273.

12 F. Pavelčík, P. Novomeský, J. Soldánová and T. Polynova, *Collect. Czech. Chem. Commun.*, 1988, **53**, 1725.

13 G. M. Sheldrich, *SHELXL93*: *Program for Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.

14 P. Schwendt, *Collect. Czech. Chem. Commun.*, 1983, **48**, 248.

15 C. Djordjevic, M. Lee-Renslo and E. Sinn, *Inorg. Chim. Acta*, 1995, **233**, 97.

16 P. Schwendt, K. Liščák and L. Ďuriš, *Chem. Pap.*, 1993, **47**, 288.

17 A. Butler, M. J. Clague and G. E. Meister, *Chem. Rev.*, 1994, **94**, 625 and references therein.

18 R. Stomberg, *Acta Chem. Scand., Ser. A*, 1984, **38**, 541 and references therein.

19 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, 1968, Vol. III.

20 A. B. Ilyukin, A. L. Poznyak and L. M. Shkolnikowa, *Koord. Khim.*, 1993, **19**, 930.

21 L. M. Shkolnikowa, K. D. Suyarow, A. A. Masyuk, A. L. Poznyak and N. M. Dyatlowa, *Koord. Khim.*, 1990, **16**, 1096.

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