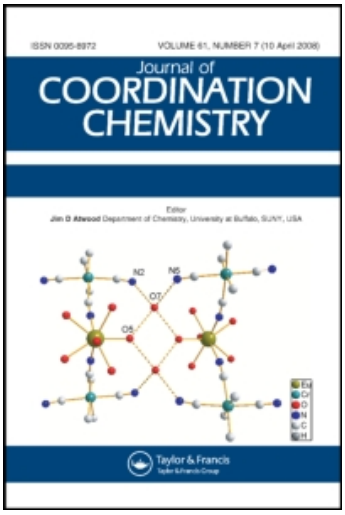

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Asymmetric dinuclear hydroxyl and ethoxyl citrato dioxovanadates(V)

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Asymmetric citrato dioxovanadates(V), $[Hneo]_4[V_2O_4(R\text{-Hcit})(OH)][V_2O_4(S\text{-Hcit})(OH)]\cdot 4H_2O$ (**1**) and $[Ni(phen)_3]_2[V_2O_4(R\text{-Hcit})(OC_2H_5)][V_2O_4(S\text{-Hcit})(OC_2H_5)]\cdot 4H_2O$ (**2**) and (H_4cit = citric acid, neo = 2,9-dimethyl-1,10-phenanthroline, phen = 1,10-phenanthroline) are isolated with the help of large counterions. Structural analyses of complexes **1** and **2** show that vanadium atoms are coordinated by tridentate citrate ligand and hydroxy or ethoxy groups, respectively. The insertions of hydroxy and ethoxy groups give new examples of the mixed RO-bridges for vanadium–citrate complexes.

Keywords: Citrate; Citric; Vanadium; Vanadate; Hydroxy; Ethoxy; Crystal structure

1. Introduction

Vanadium and citric acid play important roles in biological processes [1–3]. There are many reports on citrate complexes [4–6], especially for the citrato dioxovanadates(V) and their conversions with pH values in solution [7–9] and solid, such as $[VO_2(H_2cit)]_2^{2-}$ [10–13], $[VO_2(Hcit)]_2^{4-}$ [14, 15], $[VO_2(cit)]_2^{6-}$ [16, 17], and vanadyl citrate complexes of $[V_2O_2(Hcit)(cit)]^{3-}$ [15, 16, 18] and $[VO(cit)]_2^{4-}$ [17, 19, 20]. Complexes of $K_4[VO(cit)]_2\cdot 6H_2O$ and $(NH_4)_6[VO_2(cit)]_2\cdot 6H_2O$ have been used for tests of insulin-mimic and the activity of sarcoplasmic reticulum Ca^{2+}-ATPase [21, 22]. Moreover, a dinuclear homocitrato dioxovanadate(V) $K_2[V_2O_4(R\text{-homocit})(S\text{-homocit})]\cdot 6H_2O$ [23] has been synthesized to mimic an early mobilized precursor in the synthesis of V-nitrogenase cofactor of $[VFe_7S_9X(R\text{-homocit})(S\text{-cys})(N\text{-Him})]$ (X = C or O) [24–26]. Reports of vanadium citrate complexes with V_2O_2 and V_2O_4 core structures are limited. No reports are found on the mixed ligand complexes of citrato vanadates and vanadyl citrates, in which hydroxyl or ethoxyl group is coordinated. In the present work, the synthesis, spectral and structural characterization of two dinuclear asymmetric citrato dioxovanadates(V) are reported containing hydroxy or ethoxy bridges, respectively.

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2. Experimental

All solvents and reagents were of commercially analytical grade and used without further purification. Deionized water was used throughout this work. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed using an EA 1110 elemental analyzer. The solid diffuse UV/Vis spectra were recorded at 293 K using a Cary 5000 UV-visible-NIR spectrophotometer in the 200–800 nm range.

2.1. *Preparation of [Hneo]$_4$[V_2O_4(R-Hcit)(OH)][V_2O_4(S-Hcit)(OH)] · 4H_2O (1)*

Potassium vanadate(V) (0.14 g, 1.0 mmol) was prepared *in situ* by dissolving V_2O_5 in an aqueous solution of KOH. To the solution was added 2,9-dimethyl-1,10-phenanathroline (0.12 g, 0.55 mmol) in 95% ethanol (10 mL) and citric acid monohydrate (0.22 g, 1.1 mmol). The pH value of the resulting solution was adjusted to 3.0 with dilute hydrochloric acid. The color of the mixture turned blue at room temperature for three days. Yellow crystals (0.13 g, yield 30%) were obtained. Anal. Calcd for [Hneo]$_4$[V_2O_4(*R*-Hcit)(OH)][V_2O_4(*S*-Hcit)(OH)] · 4H_2O (**1**) (%): C, 49.4%; H, 4.4%; N, 6.8%. Found: C, 49.9%; H, 4.7%; N, 6.8%. IR (KBr, cm^{-1}): ν(COOH), 1724s; ν_{as}(COO), 1638vs, 1602vs, 1537m; ν_s(COO), 1390s, 1353m; ν(V=O), 953s 920s; ν(V–O–V), 867s; ν(V–OR), 548m, 439w.

2.2. *Preparation of [Ni(phen)$_3$]$_2$[V_2O_4(R-Hcit)(OC_2H_5)][V_2O_4(S-Hcit)(OC_2H_5)] · 4H_2O (2)*

[Ni(phen)$_3$]Cl_2 was prepared *in situ* by dissolving $NiCl_2 \cdot 6H_2O$ (0.25 g, 1.1 mmol) and 1,10-phenanthroline (0.64 g, 3.2 mmol) in 10 mL 95% ethanol. To the resulting purple-red solution was added ammonium metavanadate (0.13 g, 1.1 mmol) and citric acid (0.67 g, 3.2 mmol) in 10 mL water. The solution turned yellow and pink solid precipitated. The precipitate was suspended in 20 mL ethanol and warmed in a 60°C water-bath for two days, giving brown block crystals (0.18 g, yield 33%). Anal. Calcd for [Ni(phen)$_3$]$_2$[V_2O_4(*R*-Hcit)(OC_2H_5)][V_2O_4(*S*-Hcit)(OC_2H_5)] · 4H_2O (**2**) (%): C, 51.1%; H, 3.6%; N, 8.1%. Found: C, 50.9%; H, 3.6%; N, 8.4%. IR (KBr, cm^{-1}): ν(COOH), 1735m; ν_{as}(COO), 1659vs, 1627s, 1586s; ν_s(COO), 1428s, 1379m; ν(V=O), 932vs; ν(V–O–V) 853s; ν(V–OR), 590m, 447m. Complexes **1** and **2** are insoluble in ethanol and water and stable in the solid state.

2.3. *X-ray crystallographic analyses*

X-ray diffraction data of **1** and **2** were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.7107$ Å) radiation at 296(2) K. Empirical absorption corrections were applied using the SADABS program. All calculations were performed using WinGX and SHELXL 97 programs [27, 28]. The structures were solved by direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were generated geometrically

Table 1. Crystal data and structure refinements for complexes **1** and **2**.

	1	**2**
Formula	$C_{68}H_{72}N_8O_{28}V_4$	$C_{88}H_{76}N_{12}Ni_2O_{28}V_4$
Molecular weight	1653.10	2070.79
Crystal color, habit	Light yellow, block	Yellow, block
Temperature (K)	298(2)	173(2)
Crystal size (mm^3)	$0.23 \times 0.13 \times 0.06$	$0.20 \times 0.20 \times 0.20$
Crystal system	Triclinic	Triclinic
Cell constants (Å, °)		
a	7.7660(6)	10.5738(4)
b	9.7800(8)	12.2516(4)
c	23.343(2)	16.9999(6)
α	91.580(1)	93.155(1)
β	96.485(2)	91.163(1)
γ	103.187(1)	99.413(1)
V ($Å^3$)	1712.5(2)	2168.4(1)
Space group	$P\bar{1}$	$P\bar{1}$
Formula units/unit cell	1	1
D_{Calcd}	1.603	1.586
$F(000)$	852	1060
μ (mm^{-1})	0.624	0.929
Radiation	Mo-Kα ($\lambda = 0.7107$ Å)	Mo-Kα ($\lambda = 0.7107$ Å)
Number of reflections measured	13668	25002
Number of reflections observed	7836 ($R_{int} = 0.0967$)	9940 ($R_{int} = 0.0609$)
Goodness-of-fit	0.982	1.028
R [$I > 2\sigma(I)$]	0.0849	0.0505
WR	0.1973	0.1162
Largest difference peak and hole (e $Å^{-3}$)	0.716, −0.399	0.723, −0.580

or located from differential Fourier maps and refined isotropically. The crystallographic data of **1** and **2** are summarized in table 1. Selected distances and bond angles are listed in table 2.

3. Results and discussion

Dinuclear citrato vanadates and their transformations have been reported, with a pH-dependent reaction pattern [10–16]. The anions in the text are shown corresponding to the compound numbers, which represent both in this description. Protonation and deprotonation in the free terminal carboxyl groups of citrate result in formation of different citrate vanadates. Isolation of hydroxy and ethoxy citrato vanadates give a new class of citrate vanadates. Complex **1** with hydroxy group was obtained directly from the reaction of vanadate and citrate at pH 3, while complex **2** with ethoxy group was isolated from an ethanol solution. The later may arise from substitution of citrato vanadate with ethanol. Noteworthy is the requirement of the large counterions in isolation of complexes **1** and **2**, respectively. While there are a wealth of reports available concerning symmetric dinuclear vanadium citrate complexes including their biological tests, such as vanadates $[VO_2(H_ncit)]_2^{2n-6}$ ($n = 0$, 1 and 2) and vanadyl complexes $[VO(H_ncit)]_2^{2n-4}$ ($n = 0$ and 1), none of these have been isolated with hydroxy or ethoxy groups. The complete speciation study in solution for the $H^+/VO_4^-/cit^{4-}$ system from ^{51}V NMR and potentiometric measurements was recorded in the

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

	1	**2**		**1**	**2**
V(1)–O(1)	1.990(3)	2.003(2)	V(2)–O(1)	1.996(3)	2.000(2)
V(1)–O(2)	1.947(3)	1.961(2)	V(2)–O(4)	1.953(4)	1.974(2)
V(1)–O(8)	1.586(4)	1.629(2)	V(2)–O(10)	1.616(4)	1.633(2)
V(1)–O(9)	1.586(4)	1.619(2)	V(2)–O(11)	1.582(4)	1.617(2)
V(1)–O(12)	1.939(4)	1.983(2)	V(2)–O(12)	1.923(4)	1.989(2)
V(1)–V(2)	3.117(1)	3.161(1)			
O(1)–V(1)–O(2)	77.8(1)	78.4(1)	O(1)–V(2)–O(4)	82.5(2)	83.9(1)
O(8)–V(1)–O(1)	128.4(2)	122.2(1)	O(1)–V(2)–O(10)	121.5(2)	124.9(1)
O(1)V(1)–O(9)	122.4(2)	128.8(1)	O(1)–V(2)–O(11)	129.7(2)	124.6(1)
O(1)–V(1)–O(12)	70.8(2)	70.2(1)	O(1)–V(2)–O(12)	70.9(1)	70.1(1)
O(2)–V(1)–O(8)	95.7(2)	97.2(1)	O(4)–V(2)–O(10)	97.0(2)	96.5(1)
O(2)–V(1)–O(9)	99.3(2)	100.8(1)	O(11)–V(2)–O(4)	96.4(2)	97.5(1)
O(2)–V(1)–O(12)	148.1(2)	148.6(1)	O(12)–V(2)–O(4)	153.2(2)	153.9(1)
O(8)–V(1)–O(9)	109.1(2)	108.8(1)	O(11)–V(2)–O(10)	108.6(2)	110.1(1)
O(8)–V(1)–O(12)	99.5(2)	99.9(1)	O(10)–V(2)–O(12)	99.7(2)	99.4(1)
O(9)–V(1)–O(12)	101.9(2)	98.4(1)	O(11)–V(2)–O(12)	98.0(2)	96.2(1)
V(1)–O(1)–V(2)	102.9(1)	104.3(1)	V(2)–O(12)–V(1)	107.6(2)	105.5(1)

pH range 2–10 [7–9, 21, 22]. The addition of hydroxy or ethoxy in citrate vanadates gives new examples of the mixed RO-bridges for the vanadium–citrate complexes, demonstrating that solvents should be considered for the species distributions of citrato vanadates in solution.

X-ray diffraction analyses revealed that **1** and **2** contain discrete dinuclear hydroxy or ethoxy citrato dioxovanadium(V) anions, protonated 2,9-dimethyl-1,10-phenanthroline or triphenanthroline nickel(II) cations and lattice water molecules. The anions in **1** and **2** consist of a V_2O_2 rhombic core with two oxygen bridges, derived from the alkoxide moieties of the citrate and hydroxy or ethoxy ligands. The two doubly bonded oxygen atoms coordinate to the vanadium atom. Opposite sites are occupied by oxygen atoms from the same citrate ligand. The citrate ion is a tridentate ligand with the central alkoxyl and carboxyl moieties coordinated to one vanadium atom, while terminal carboxyl group coordinates to the other vanadium atom, leaving the other terminal carboxyl group free. The angles of the V–O–V bridges are similar to those found in citrate vanadates(V) $[VO_2(H_2cit)]_2^{2-}$ [10, 11], $[VO_2(Hcit)]_2^{4-}$ [13, 15] and $[VO_2(cit)]_2^{6-}$ [15–17]. Each vanadium atom is five coordinate with a distorted trigonal-bipyramidal geometry. The achiral citrate ligand exhibits a chiral center due to the asymmetric coordination to the vanadium atom. Both the *R*- and *S*-Hcit vanadates exist in the cell. Only *R* or *S*-configuration of citrate complexes are shown in figures 1 and 2.

In **1** and **2**, the V–O distances in citrato vanadates vary systematically. The V=O range is 1.582(4)–1.633(2) Å, indicating double bonds. The V···V distance for **1** and **2** are 3.117(1) and 3.161(1) Å, respectively, shorter than those of the symmetric dinuclear V_2O_2 units in the range of 3.225–3.265 Å. This is because the hydroxy and ethoxy groups are smaller than citrate. The V–O bond distances in **1** and **2** are similar with corresponding distances in citrato dioxovanadium(V) complexes, and shorter than those in the dinuclear vanadyl citrate as shown in table 3. The V–O bonds of hydroxy and ethoxy groups are shorter than those of α-alkoxy groups due to the size of citrate. The citrate ligands of **1** and **2** adopt extended conformation upon binding to the vanadium ions. The carbon atoms of C(1), C(2), C(3), C(4) and C(1), C(3), C(5), C(6)

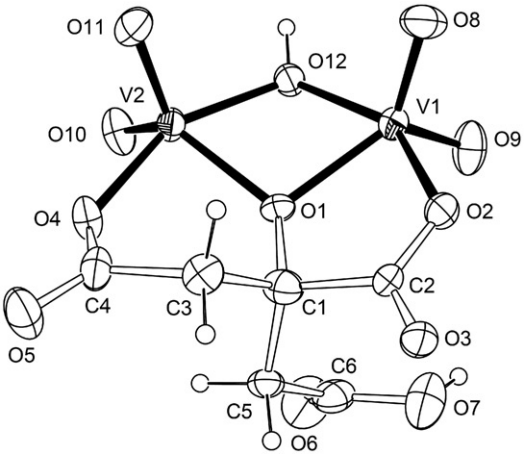

Figure 1. ORTEP plot of the *R*-anion structure for $[Hneo]_4[V_2O_4(R\text{-Hcit})(OH)][V_2O_4(S\text{-Hcit})(OH)] \cdot 4H_2O$ (**1**) at the 30% probability level.

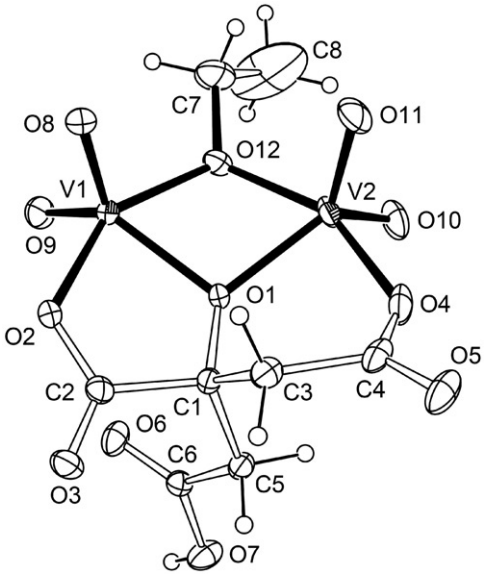

Figure 2. ORTEP plot of the *S*-anion structure for $[Ni(phen)_3]_2[V_2O_4(R\text{-Hcit})(OC_2H_5)][V_2O_4(S\text{-Hcit})(OC_2H_5)] \cdot 4H_2O$ (**2**) at the 30% probability level.

of the citrate backbones are coplanar. The torsional angles of C(1), C(2), C(3), C(4) are 5.8 and 4.4°, and those of C(1), C(3), C(5), C(6) are 1.8 and 10.3° for **1** and **2**, respectively. Evidently, the bridged oxygen in **1** is protonated, shown by the presence of hydrogen in difference maps, by its distance to vanadium [V1–O12 1.939(4), V2–O12 1.923(4) Å], and from the charge balance.

The anions of complex **2** have hydrophilic and hydrophobic ends and pack as hydrophilic with hydrophilic or hydrophobic with hydrophobic. The cations are composed of Ni(II) and three phenanthroline ligands in an octahedral configuration.

Table 3. Comparisons of V–O bond distances (Å) in citrato vanadates.

V^{n+}	Complexes	V–O (α-alkoxyl)	V–O (α-carboxyl)	V–O (β-carboxyl)	V–OR [R = H, C_2H_5]	Ref.
+5	$[Hneo]_4[V_2O_4(R\text{-Hcit})(OH)][V_2O_4(S\text{-Hcit})(OH)]\cdot 4H_2O$ (**1**)	1.990(3), 1.996(3)	1.947(3)	1.953(4)	1.939(4), 1.923(4)	
	$[Ni(phen)_3]_2[V_2O_4(R\text{-Hcit})(OC_2H_5)]\ [V_2O_4(S\text{-Hcit})(OC_2H_5)]\cdot 4H_2O$ (**2**)	2.003(2), 2.000(2)	1.961(2)	1.974(2)	1.983(2), 1.989(2)	This work
	$K_2[VO_2(H_2cit)]_2\cdot 4H_2O$	1.961(3), 2.010(4)	1.980(3)			[10]
		1.957(2), 2.013(2)	1.980(2)			[11]
		1.966(3), 2.005(3)	1.976(4)			
	$Na_2K_2[V_2O_4(Hcit)_2]\cdot 9H_2O$	1.973(4), 1.993(3)	1.982(4)			[14]
+5		1.970(2), 2.017(2)	1.966(2)			
	$K_4[V_2O_4(Hcit)_2]\cdot 5.6H_2O$	1.974(3), 2.005(3)	1.977(3)			[15]
	$(NH_4)_4[V_2O_4(Hcit)_2]\cdot 4H_2O$	1.968(1), 2.026(1)	1.977(2)			[16]
	$(NH_4)_6[V_2O_4(cit)_2]\cdot 6H_2O$	1.964(2), 2.004(1)	1.981(2)			[16]
	$K_2(NH_4)_4[V_2O_4(cit)_2]\cdot 6H_2O$	1.961(2), 2.005(2)	1.981(2)			[17]
	Average	1.987	1.976			
		1.964(2), 2.194(2)	2.043(2)	2.029(2), 2.018(2)		
+4	$(NH_4)_4[VO_2(cit)]_2\cdot 2H_2O$	1.956(2), 2.192(2)	2.055(2)	2.018(2), 2.052(2)		[19]
	$Na_4[VO_2(cit)]_2\cdot 12H_2O$	1.986(2), 2.230(2)	2.039(2)	2.030(2), 2.003(2)		[19]
	$Na_4[VO_2(cit)]_2\cdot 6H_2O$	1.971(2), 2.206(2)	2.038(2)	2.032(2), 2.017(2)		[17]
	$K_4[VO_2(cit)]_2\cdot 6H_2O$	1.977(3), 2.171(3)	2.041(3)	1.992(3), 2.022(3)		[20]
	Average	2.085	2.043	2.021		

The π–π stacking between two phen ligands of two $[Ni(phen)_3]^{2+}$ moieties in **2** are shown in figure S3(b). The two phen are parallel to each other, and only one arene ring of each phen is involved in π–π stacking. They interact in an offset or parallel-displaced mode [29]. The centroid–centroid distance is 3.753 Å and the displacement angle is 0°. The anions and the cations fill each interspace. Each anion is surrounded by four cations, while each cation has four anions. The BVS calculation about V(1) and V(2) are 5.560, 5.455 in **1** and 5.105, 5.046 in **2** respectively [30], so the valences of vanadium atoms in **1** and **2** are +5.

The solid diffuse UV-Vis spectra of **1** and **2** show absorptions at 258, 315, 356, 500 and 219, 256, 295, 327, 515 nm, respectively. The absorptions of 500 and 515 nm could be assigned for d–d transitions of citrato vanadates, and the features below 360 nm could be reasonably attributed to charge-transfer or $\pi \rightarrow \pi$ bands [31]. The FT-infrared spectra of **1** and **2** confirm the presence of carboxyl groups with antisymmetric and symmetric vibrations of the coordinated citrate ligands. Hence, antisymmetric stretching vibrations ν(COO) were present for the carboxyl carbonyls in the range 1690–1650 and 1640–1570 cm^{-1} for **1** and **2**, respectively. Symmetric vibrations ν(COO) were present around 1400 cm^{-1} for both **1** and **2** [32]. The difference between the symmetric and antisymmetric stretches $\Delta[\nu(COO) - \nu(COO)]$ was greater than 200 cm^{-1}, indicating that the citrate carboxyl groups were either free or coordinated to vanadium in a monodentate fashion. Confirmation of the latter assessment was provided by the X-ray crystal structures. The ν(V=O) vibrations for the VO_2^+ groups in **1** and **2** were present in the range 945–868 cm^{-1}. The above described tentative assignments were in agreement with previous assignments in dinuclear V(V) complexes [10–17].

4. Conclusions

The solid complexes isolated with large counterions show citrato vanadates coordinated with hydroxy and ethoxy from the solvent of the reactions, which is important for understanding the species distribution of vanadium(V)–citrate complexes. Concomitantly, due to the complexity of the citrato vanadate system, it is difficult to completely define all of the related species. The study of the ternary vanadium-ligand system might be useful for the study of the other species distributions of citrato vanadates in solution.

Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. 292637 and 281336. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version.

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References

[1] R.Wewer, M.B.E. Kreenn. In *Vanadium in Biological Systems*, N.D. Chasteen (Ed.), Kluwer Academic Publishers, Dordrecht (1990).
[2] J.P. Glusker. *Acc. Chem. Res.*, **13**, 345 (1980).
[3] D.C. Crans, J.J. Smee, E. Gaidamauskas, L.Q. Yang. *Chem. Rev.*, **104**, 849 (2004).
[4] Z.H. Zhou, Y.J. Lin, H.B. Zhang, G.D. Lin, K.R. Tsai. *J. Coord. Chem.*, **42**, 131 (1997).
[5] P. Che, D.Q. Fang, D.P. Zhang, J. Feng, J.P. Wang, N.H. Hu, J. Meng. *J. Coord. Chem.*, **58**, 1581 (2005).
[6] J.Q. Xu, D.M. Li, Y.H. Xing, R.Z. Wang, S.Q. Liu, T.G. Wang, Y. Xing, Y.H. Lin, H.Q. Jia. *J. Coord. Chem.*, **53**, 25 (2001).
[7] P.M. Ehde, I. Andersson, L. Pettersson. *Acta Chem. Scand.*, **43**, 136 (1989).
[8] T. Kiss, P. Buglyo, D. Sanna, G. Micera, P. Decock, D. Dewaele. *Inorg. Chim. Acta*, **239**, 145 (1995).
[9] A. Gorzás, K. Getty, I. Andersson, L. Pettersson. *Dalton Trans.*, 2873 (2004).
[10] Z.H. Zhou, W.B. Yan, H.L. Wan, K.R. Tsai, J.Z. Wang, S.Z. Hu. *J. Chem. Crystallogr.*, **25**, 807 (1995).
[11] D.W. Wright, P.A. Humiston, W.H. Orme-Johnson, W.M. Davis. *Inorg. Chem.*, **34**, 4194 (1995).
[12] M. Tsaramyrsi, D. Kavousanaki, C.P. Raptopoulou, A. Terzis, A. Salifoglou. *Inorg. Chim. Acta*, **320**, 47 (2001).
[13] M. Kaliva, E. Kyriakakis, A. Salifoglou. *Inorg. Chem.*, **41**, 7015 (2002).
[14] Z.H. Zhou, H. Zhang, Y.Q. Jiang, D.H. Lin, H.L. Wan, K.R. Tsai. *Trans. Met. Chem.*, **24**, 605 (1999).
[15] M. Kaliva, T. Giannadaki, A. Salifoglou. *Inorg. Chem.*, **41**, 3850 (2002).
[16] M. Kaliva, C.P. Raptopoulou, A. Terzis, A. Salifoglou. *J. Inorg. Biochem.*, **93**, 161 (2003).
[17] Z.H. Zhou, H.L. Wan, S.Z. Hu, K.R. Tsai. *Inorg. Chim. Acta*, **237**, 193 (1995).
[18] S. Burojevic, I. Shweky, A. Bio, D.A. Summers, R.C. Thompson. *Inorg. Chim. Acta*, **251**, 75 (1996).
[19] M. Tsaramyrsi, M. Kaliva, A. Salifoglou, C.P. Raptopoulou, A. Terzis, V. Tangoulis, J. Giapintzakis. *Inorg. Chem.*, **40**, 5772 (2001).
[20] M. Velayutham, B. Varghese, S. Subramanian. *Inorg. Chem.*, **37**, 1336 (1998).
[21] D. Rehder, J.C. Pessoa, C.F.G.C. Geraldes, M.M.C.A. Castro, T. Kabanos, T. Kiss, B. Meier, G. Micera, L. Pettersson, M. Rangel, A. Salifoglou, I. Turel, D.R. Wang. *J. Biol. Inorg. Chem.*, **7**, 384 (2002).
[22] M. Aureliano, T. Tiago, R.M.C. Gândara, A. Sousa, A. Moderno, M. Kaliva, A. Salifoglou, R.O. Duarte, J.J.G. Moura. *J. Inorg. Biochem.*, **99**, 2355 (2005).
[23] D.W. Wright, R.T. Chang, S.K. Mandal, W.H. Armstrong, W.H. Orme-Johnson. *J. Biol. Inorg. Chem.*, **1**, 143 (1996).
[24] O. Einsle, F.A. Tezcan, S.L.A. Andrade, B. Schmid, M. Yoshida, J.B. Howard, D.C. Rees. *Science*, **297**, 1696 (2002).
[25] T.C. Yang, N.K. Maeser, M. Laryukhin, H.I. Lee, D.R. Dean, L.C. Seefeldt, B.M. Hoffman. *J. Am. Chem. Soc.*, **127**, 12804 (2005).
[26] R.R. Eady. *Coord. Chem. Rev.*, **237**, 23 (2003).
[27] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).
[28] G.M. Sheldrick. *SHELX-97, Programs for Crystal Structure Analysis*, University of Göttingen, Germany (1999).
[29] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[30] N.E. Brese, M. O'Keeffe. *Acta Cryst.*, **B47**, 192 (1991).
[31] M. Ferbinteanu, F. Cimpoesu, M. Andruha, F.D. Rochon. *Polyhedron*, **21**, 2560 (1998).
[32] G.B. Deacon, R. Philips. *Coord. Chem. Rev.*, **33**, 227 (1980).