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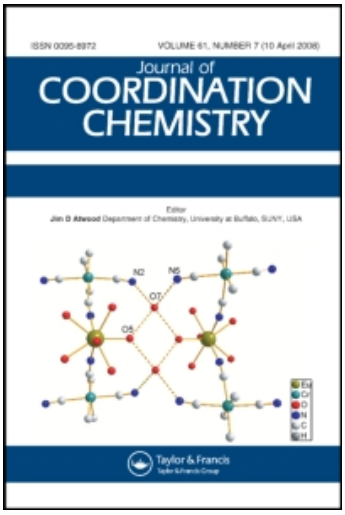

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Syntheses, Characterization and Stereochemistry of S - and R , S - Hydrogenmalato Dioxotungsten(VI)

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SYNTHESES, CHARACTERIZATION AND STEREOCHEMISTRY OF *S*- AND *R,S*-HYDROGENMALATO DIOXOTUNGSTEN(VI)

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Cis-dioxo hydrogenmalato tungstates(VI) Δ-$Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$ **1**, and $Na_2[WO_2(R,S\text{-Hmal})_2]$**2** ($H_3$mal = malic acid) have been prepared from the reactions of excess *S*-malic acid and *R,S*-malic acid respectively, with sodium tungstate at ambient temperature. Both complexes were characterized by elemental analyses, conductivity measurement, optical rotation, UV-Vis, IR and NMR spectroscopy. Complex **1** was obtained with predetermined helical chirality at the metal center for a Δ-*cis*-configuration, which is established by single crystal X-ray diffraction. The crystal is orthorhombic, space group $P2_12_12_1$, with unit cell parameters: $a = 7.9545(6)$, $b = 10.7440(8)$, $c = 21.045(2)$Å, $V = 1798.6(2)$Å^3, $Z = 4$, $D_c = 2.215\,g\,cm^{-3}$, $F(000) = 1152$, $R = 0.031$, $R_w = 0.034$. Single crystal X-ray diffraction reveals that the *cis*-dioxo tungstate **1** is octahedrally coordinated by the *S*-malate through the deprotonated α-hydroxy and α-carboxylate groups, while the β-carboxylic acid groups remain uncomplexed.

Keywords: Tungstate(VI); Tungsten; Malic acid; Malate; Stereochemistry; Chirality; Crystal structure

INTRODUCTION

Tungsten is the active center of some enzymes. It was found that this metal can have a positive biological role, contrary to the traditional view of tungsten as an antagonist of the biological function of Mo [1]. The first indication was the reported use of tungstates to stimulate the growth of certain acetate- and methane-producing microorganisms [2,3], but it was not until 1983 that the first naturally occurring tungstoenzyme was purified from one of the acetogens [4]. Tungsten is present in microbial enzymes like the formate dehydrogenase from clostridium thermoaceticum [4,5]. Research on tungsten coordination chemistry has drawn much attention through studies of tungstate complexes of hydroxycarboxydrate ligands like gluconic acid, glycolic, D-galactaric acid, D-glycero-D-gulo-heptonic acid, L-mannonic acid and citric acid [6–10]. Many hexacoordinate dioxotungsten complexes relevant to tungstoenzyme systems have

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been structurally characterized, i.e. $WO_2(R_2dtc)_2$ (R = Et, Me; dtc = dithiocarbamate) [11,12], and also other oxo tungstates [13,14].

Metal-hydroxycarboxylate complexes are typical for citrato or malato tungsten and molybdenum systems [15–24]. In particular, the model does not differ much from that obtained for molybdenum(VI) with malate or citrate as a ligand. Proton NMR spectroscopy of W(Mo)-malate demonstrates the existence of four complexes 1 : 1, 2 : 1 and two 1 : 2 species. It is proposed that the tungsten complexes are more stable than the analogous molybdenum complexes. Previous investigations of the complexation of tungsten(VI) with malate have shown the presence of complexes having 1 : 1, 2 : 2, 2 : 1, and 1 : 2 tungstate : malate stoichiometries [16]. In this work, we report on the syntheses and characterization of *S*- and racemic malato tungsten(VI) complexes from a weakly acidic solution. The absolute configuration of the resultant malato tungstate $Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$ **1** (malic acid = H_3mal) is assigned as Δ.

EXPERIMENTAL

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All reagents are commercially available. Electronic spectra were recorded on a UV-360 spectrophotometer and infrared spectra as Nujol mulls between KBr plates on a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed using EA 1110 elemental analyzers. Conductometric measurements were performed on DDS-11A conductometer. The optical rotation in water was measured on a WZZ-I polarimeter. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY 500 NMR spectrometer using DDS as internal reference.

Preparation of *cis*-$Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$

Sodium tungstate (20 mmol) was added to a solution of excess *S*-malic acid (44 mmol). The mixture (pH 2) was heated in a water bath at 60°C for 5 h. The resultant solid was collected and washed with ethanol to give a white solid (6.0 g, 50%). Anal. Calcd. for $C_8H_{16}O_{16}Na_2W_1$(%):C, 16.1, H, 2.7 found: C, 16.4, H, 2.7. Specific rotary power: $[\alpha]_D^{20}$ −27.6° (H_2O, *c* 18.5). IR (KBr): ν_{as} (C=O) 1729_s, $1680_{s,sh}$, 1650_{vs}, $1629_{s,sh}$, ν_s (C=O) 1427_s, 1399_s, 1370_s, 1350_s,ν(W=O) 948_s, 900_s, 883_s cm^{-1}. ^{1}H NMR (500 MHz, D_2O, ppm) δ_H: 5.348 (1H, m), 2.816 (2H, m). ^{13}C NMR (D_2O, ppm) δ: 184.6 $(CO_2)_\alpha$,174.7 $(CO_2)_\beta$, 79.8 $(C–O)_\alpha$, 38.8(CH_2).

Preparation of *cis*-$Na_2[WO_2(R,S\text{-Hmal})_2]$

The same procedure was followed as for *cis*-$Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$ except that racemic malic acid was used in place of *S*-malic acid. The solid was collected and washed with ethanol to give a white solid (6.6 g, 55%). Anal. Calcd. for $C_8H_8O_{12}Na_2W_1(\alpha_a)$:C, 18.3, H, 1.5, Found: C, 18.4, H, 1.7. It has no specific rotary power. IR (KBr): ν_{as} (C=O) 1723_s, $1685_{s,sh}$, 1652_{vs}, ν_s (C=O) 1425_s, 1400_s, $1385_{s,sh}$, ν (W=O) 930_s, 911_s, 867_{vs}, 826_s, cm^{-1}.

Crystals of suitable quality for the subsequent X-ray diffraction studies were obtained as transparent prisms by cooling the saturated solution of the compounds in a refrigerator. The resulting colorless crystals were mounted in a capillary for X-ray analysis.

TABLE 1 Crystal data summaries of intensity data collection and structure refinement for Δ-$Na_2[WO_2(S\text{-Hmal})_2 \cdot 4H_2O$ **1**

Formula	$C_8H_{16}O_{16}Na_2W_1$
Molecular weight	598.04
Crystal color, habit	Colorless, needle
Crystal size (mm)	$0.22 \times 0.22 \times 0.38$
Crystal system	orthorhombic
Cell constants:	$a = 7.9545(6)$ Å $b = 10.7440(8)$ Å $c = 21.045(2)$ Å $V = 1798.6(2)$ Å^3
Space group	$P2_12_12_1$
Formula units/unit cell	4
D_{calc}	2.215
F_{000}	1152
μ (Mo Kα)	66.8
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo Kα ($\lambda = 0.7107$ Å)
Number of reflections measured	2035
Number of reflections observed	1823
$[I > 3\sigma(I)]$[a]	($R_{int} = 0.030$)
Flack parameter	$-0.04(3)$
Number of parameters varied	245
Weighting scheme (w =)	$[\sigma(F_o)^2 + 0.0001(F_o)^2 + 1]^{-1}$
Goodness of fit	0.38
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.031
R_w	0.034
Largest difference peak and hole (e · Å^{-3})	0.82, -0.17

[a]Corrections: Lorentz-polarization.

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X-ray Data Collection, Structure Solution and Refinement

A crystal of compound **1** was measured on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo-Kα radiation at 296 K. A total of 25 reflections with $2^\circ < 2\theta < 52^\circ$ were collected through a random search routine and indexed using the principle of shortest vectors followed by least-squares refinement. A total of 2035 reflections were collected, with the ω-2θ scan mode adopted for data collection, of which 1823 reflections had intensities with $I > 3\sigma(I)$. Lp factor, anisotropic decay and empirical absorption corrections were applied. The primary structure was solved by WinGX package [25] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the nonhydrogen atoms. H atoms were located from a difference Fourier map and not refined. Final calculations were performed on a PC microcomputer using MoLEN software [26] and published scattering factors [27] (Table I).

RESULTS AND DISCUSSION

The stoichiometry of the reactants and pH are crucial for product formation (pH 2–3). Depending mainly on the requisite proportions, the title compounds were prepared by the reactions of sodium tungstate and *S*-malic acid or racemic malic acid in the ratio of 1 : 2. The separated products with insufficient malic acid are only the homopolytungstates(VI). Further increase in pH resulted in the formation of polymeric malato tungstate(VI) $Na_3[WO_2H(S\text{-mal})_2]$ [24]. The preferred stoichiometry of the

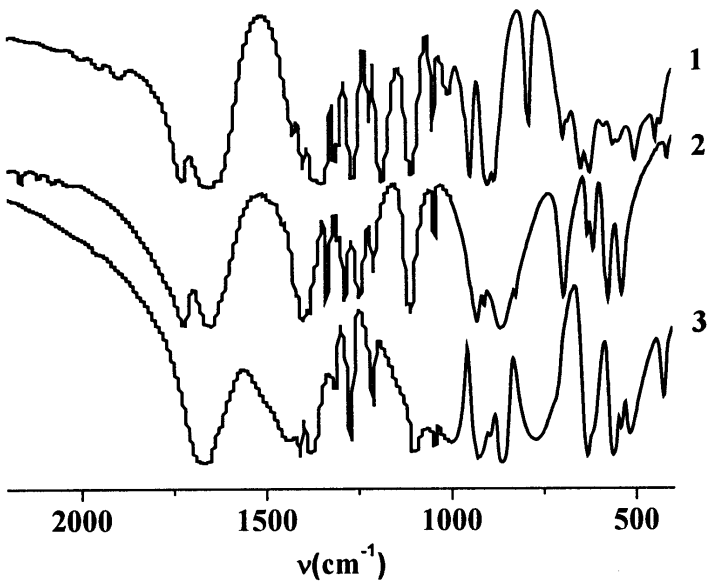

FIGURE 1 IR spectra of $Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$ (top), $Na_2[WO_2$ $(R,S\text{-Hmal})_2]$ (middle), and $Na_3[WO_2H(S\text{-mal})_2]$ (bottom).

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product is 1 : 2 for metal-to-ligand ratio, which is more stable than 1 : 1, 2 : 2 and 2 : 1 complexes [16].

The tungsten(VI) complexes are featureless in the visible range 350–600 nm. The two tungstates show similar patterns of IR spectra in the region between 1800 and 1400 cm^{-1}, in which the bands of 1729_s, $1680_{s,sh}$, 1650_{vs}, $1629_{s,sh}$, and 1427_s, 1399_s, 1370_s, 1350_s cm^{-1} (**1**), 1723_s, $1685_{s,sh}$, 1652_{vs}, and 1425_s, 1400_s, $1385_{s,sh}$, cm^{-1} (**2**) correspond to the bound carboxylic and carboxylate groups ν_{as} and ν_s, (CO_2), respectively. This is in accord with the coordinated and free carboxylic group of the malato ligands. The latter forms strong hydrogen bonding between carboxylic and carboxylate groups. Both complexes show several bands which result from the presence of W=O in the region between 950–830 cm^{-1}. Figure 1 shows the IR spectra of different malato tungstates (VI) $Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$ **1**, $Na_2[WO_2(R,S\text{-Hmal})_2]$ **2** and Na_3 $[WO_2H(S\text{-mal})_2]$ **3**. The molar electrical conductivities of compounds **1** and **2** are 1.48×10^{-2} and 1.62×10^{-2} $S\,m^2\,mol^{-1}$, close to that expected for a bivalent coordinated anion [28]. Compounds **1** and **2** have similar structures to $Na_2[WO_2(Hmal)_2]$. Compound **1** has rotary power while compound **2** has not, which might form a mixture of diastereoisomers like $\Lambda(R,R)$, $\Delta(S,S)$, $\Lambda(S,S)$, $\Delta(R,R)$, $\Lambda(R,S)$ and $\Delta(S,R)$. The chiral Δ-configuration in compound **1** is achieved through enantiopure chiral *S*-malate ligands. The decomposition of compound **1** with hydrogen chloride results in the isolation of *S*-malic acid, which implies the retention of configuration of the ligand after complexation.

The ^1H NMR spectrum of the well formed crystals of **1** shows obvious low-field shift ($\Delta\delta = 0.966$ ppm) of the α-hydrogen, and no obvious shift of the β-hydrogen in malate is observed compared with potassium hydrogen malate at the same pH, implying coordination of α-alkoxy and α-carboxy groups. The potassium hydrogen malate displays three isolated quartets with 4.382 ($J = 4.5$, 8.0 Hz), 2.813 ($J = 4.0$, 16.0 Hz)

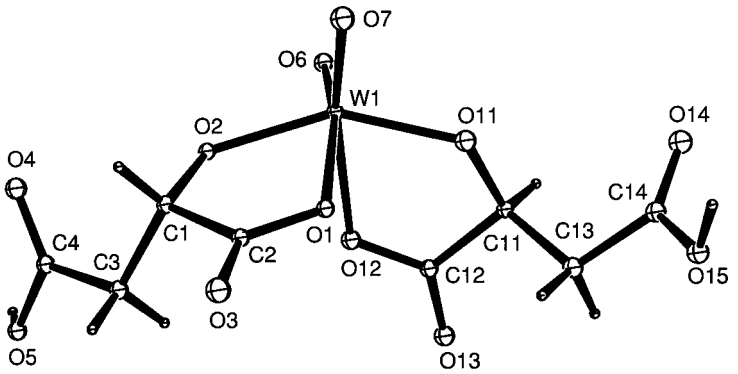

FIGURE 2 Perspective view of the anion structure of Δ-$Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$.

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and 2.641 ppm ($J = 8.0$, 16.0 Hz). The large low-field shift of some ^{13}C resonances clearly supports that both alkoxy ($\Delta\delta$ 11.3 ppm) and α-carboxy ($\Delta\delta$ 5.6 ppm) groups are coordinated. A small shift of β-carboxy group ($\Delta\delta$ 1.4 ppm) is consistent with the free terminal carboxylic groups revealed by X-ray crystallography.

A complete X-ray structural determination reveals that the crystal structure of Δ $Na_2[WO_2(S\text{-Hma1})_2]\cdot 4H_2O$ **1** consists of discrete sodium cations, hydrogen dimalato dioxotungstate anions and crystal water molecules. Figure 2 shows a perspective view of the complexed anion. The tungsten(VI) atoms are six-coordinate with two unshared terminal *cis*-oxygen groups and two protonated malate ligands, which exist in *quasi*-octahedral geometry. Each malate ion acts as a bidentate ligand with the alkoxy and α-carboxyl coordinated to one tungsten atom, and the other β-carboxylic acid groups remain uncomplexed. The product is isostructural with the molybdate(VI) congerner complex of malate $Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$ [29]. This is similar to the coordination mode of homocitate to molybdenum in the FeMo cofactor [30].

Selected atomic distances and bond angles are given in Table II. The W=O distances are shortest [1.735(8), 1.752(8) Å], indicating that they are double bonds. The resulting O=W=O angle, 105.2(4)° is considerably larger than the 90° regular value, which is expected from the greater O···O repulsions between oxygens with short bonds to the metal atom. The W–O (α-alkoxy) distances are longer [1.950(7), 1.954(7) Å], which show the deprotonation of the hydroxyl group in the malate anion, different with malato or citrato complexes of nickel(II) [31,32]. Those W–O distances to α-carboxyl are longest [2.222(8), 2.185(7) Å], which might be the result of the strong *trans*-influence. The observed C–O distances of terminal β-carboxyl groups with protons are inequivalent [O(4)–C(4), 1.22(1) Å and O(5)–C(4), 1.30(1) Å; O(14)–C(14), 1.20(1) Å and O(15)–C(14), 1.32(1) Å]. There is strong intermolecular hydrogen bonding between protonated and deprotonated carboxyl groups [O(1)–O(5a), 2.61(1); O(12)–O(15b), 2.58(1) Å].

For comparison, some related M–O (M=W and Mo) bond distances of citrato and malato complexes are listed in Table III. Due to the lanthanide contraction, the structure of compounds containing molybdenum and tungsten are very similar.

The *cis*-dioxo compounds of $Na_2[MO_2(S\text{-Hmal})_2]\cdot 4H_2O$, $Na_3[MO_2H(S\text{-mal})_2]$ and $Na_2[MO_2(H_2cit)_2]\cdot 3H_2O$ (M = Mo or W) have some similarities, although the *trans*-monomers are also seen in complexes like *trans*-$[Mn(R,S\text{-}H_2mal)_2(H_2O)_2]\cdot H_2O$

TABLE II Selected bond distances (Å) and angles (°) for Δ-$Na_2[WO_2(S\text{-Hmal})_2]\cdot 4H_2O$

W(l)–O(1)	1.950(7)	W(1)–O(2)	2.222(8)
W(1)–O(11)	1.954(7)	W(1)–O(12)	2.185(7)
W(l)–O(6)	1.735(8)	W(l)–O(7)	1.752(3)
O(l)–W(1)–O(2)	74.2(3)	O(1)–W(1)–O(6)	94.1(3)
O(1)–W(l)–O(7)	104.7(3)	O(1)–W(1)–O(11)	149.5(3)
O(1)–W(1)–O(12)	81.9(4)	O(2)–W(1)–O(6)	165.3(3)
O(2)–W(1)–O(7)	86.7(3)	O(2)–W(1)–O(11)	83.1(3)
O(2)–W(1)–O(12)	79.8(3)	O(6)–W(1)–O(7)	105.2(4)
O(6)–W(1)–O(11)	104.3(3)	O(6)–W(1)–O(12)	89.9(3)
O(7)–W(1)–O(11)	93.7(3)	O(7)–W(1)–O(12)	162.8(3)
O(11)–W(1)–O(12)	74.3(3)		
Hydrogen bonding			
O(1)...O(5a)	2.61(1)	O(12)...O(15b)	2.58(1)
O(3)...O(16c)	2.79(1)	O(4)...O(10d)	2.97(1)
O(7)...O(16e)	2.83(1)	O(8)...O(10f)	2.81(1)
O(9)...O(13g)	2.61(1)	O(9)...O(16h)	2.72(2)

a (1 + *x*, *y*, *z*), *b* (−1 + *x*, *y*, *z*), *c* (−1/2 + *x*, 1/2 − *y*, −*z*), *d* (−1/2 + *x*, 3/2 − *y*, 1 −*z*), *e* (1/2 − *x*, −*y*, 1/2 + *z*), *f* (1 − *x*, −1/2 + *y*, 1/2−*z*), *g* (1/2 + *x*, 3/2 − *y*, 1 −*z*), *h* (1/2 + *x*, 1/2−*y*, 1−*z*).

TABLE III Comparisons of M–O distances (Å) (M = Mo, W) in malato and citrato complexes

Compound	*M–O(alkoxy)*	*M–O(α-carboxy)*	*Reference*
$Cs_2[MoO_2(S\text{-Hmal})_2]\cdot H_2O$	1.939(8)	2.243(9)	23
$Na_2[MoO_2(S\text{-Hmal})_2]\cdot 4H_2O$	1.946(4), 1.950(4)	2.203(4), 2.223(5)	29
$Na_2[WO_2(S\text{-HMal})_2]\cdot 4H_2O$	2.02(3), 1.95(3)	2.21(3), 2.17(4)	This work
$Na_3[MoO_2H(S\text{-mal})_2]$	1.935(2)	2.182(2)	33
$Na_3[WO_2H(S\text{-mal})_2]$	1.973(4)	2.170(4)	24
$Na_2[MoO_2(H_2cit)_2]\cdot 3H_2O$	1.953(6), 1.960(7)	2.190(7), 2.247(6)	22
$Na_2[WO_2(H_2cit)_2]\cdot 3H_2O$	1.945(6), 1.968(7)	2.189(8), 2.227(7)	22

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[34]. The *cis*-dioxo species are the main products of the malato tungstates and molybdates. Transformations between *cis*-dioxo molybdate or tungstate complexes can be accomplished by controlling the pH as for dimeric peroxo malatovanadates [35].

$$cis\text{-}[MO_2(Hmal)_2]^{2-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} cis\text{-}[MO_2H(mal)_2]^{3-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} cis\text{-}[MO_2(mal)_2]^{4-} (M = Mo, W)$$

An enantioselective aggregation with homochirality -ΔΔΔ- or -ΛΛΛ- is obtained within a one or two dimensional catenarian chain through strong hydrogen bonding, resulting in formation of homochiral supramolecular entities from chiral components in $Na_2[WO_2(S\text{-Hmal})_2]$ and $Na_3[WO_2H(S\text{-mal})_2]$. The metal centers of the *S*-malato molybdates and tungstates have chiralities induced by the *S*-malate. The configuration of $Na_3[WO_2H(S\text{-mal})_2]$ is Λ, while $Na_2[WO_2(S\text{-Hmal})_2]$ is Δ. The formation of homochiral polymeric malato tungstates are due to the different solubilities of diastereoisomers.

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Supplementary Data

Atomical coordinates, thermal parameters, and a full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre under CCDC no. 170378. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam. ac.uk). Computed and observed structure factor moduli, along with infrared and electron absorption data can be obtained from the authors.

References

[1] M.K. Johnson, D.C. Rees and M.W.W. Adams, *Chem, Rev*. **96**, 2817 (1996).
[2] J.R. Andreesen and L.G. Ljungdahl, *J. Bacteriol*. **116**, 867 (1973).
[3] J.R. Andreesen and L.G. Ljungdahl, *J. Bacteriol*. **120**, 6 (1974).
[4] L. Yamamoto, T. Saiki, S.M. Liu and L.G. Ljvngdahl, *J. Biol. Chem*. **258**, 1826 (1983).
[5] C.N. Durfor, P.J. Wetherbee, J.C. Deaton and E.I. Solomon, *Biochem. Biophys. Res. Commun*. **115**, 61 (1983).
[6] M.L. Ramos, M.M. Caldeira, V.M.S. Gil, H. Vanbekkum and J.A. Peters, *J. Coord. Chem*. **33**, 319 (1994).
[7] M. Hlaibi, M. Benaissa, C. Busatto, J.F. Verchere and S. Chapelle, *Carbohydrate Res*. **278**, 227 (1995).
[8] M.L. Ramos, M. M. Caldeira and V.M.S. Gil, *Carbohydrate Res*. **299**, 209 (1997).
[9] M.L. Ramos and M.M. Caldeira, *Inorg. Chim. Acta* **180**, 219 (1991).
[10] M.M. Caldeira, M.L. Ramos, V.M.S. Gil, H. Van Bekkum and J.A. Peters, *Inorg. Chim. Acta* **221**, 69 (1994).
[11] S.B. Yu and R.H. Holm, *Inorg. Chem*. **28**, 4385 (1989).
[12] G.J. Chen, J.W. Mcdonald and W.E. Newton, *Inorg. Chem. Acta* **19**, 67 (1976).
[13] L. Xu, Z.F. Li, H. Liu and J.S. Huang, *J. Coord. Chem*. **40**, 133 (1996).
[14] J.L Atwood, S.G. Bott, P.C. Junk and M.T. May, *J. Coord. Chem*. **37**, 89 (1996).
[15] J.J. Cruywagen, E.A. Rohwe and R.F. Van de Water, *Polyhedron* **16**, 243 (1997).
[16] J.J. Cruywagen, L. Krüger and E.A. Rohwer, *J. Chem. Soc. Dalton Trans*. 1925 (1997).
[17] J.J. Cruywagen, E.A. Rohwes and G.F.S. Wessels, *Polyhedron* **14**, 3481 (1995).
[18] J.J. Cruywagen, L. Krüger and E.A. Rohwer, *J. Chem. Soc. Dalton Trans*. 1927 (1991).
[19] E. Llopis, J.A. Ramirez, A. Doménech and A. Cervilla, *J. Chem. Soc. Dalton Trans*. 1121 (1993).
[20] J.J. Cruywagen, L.J. Saayman and M.L. Niven, *J. Crystallogr. Spectrosc. Res*. **22**, 737 (1992).
[21] J.Q. Xu, D.M. Li, Y.H. Xing, R.Z. Wang, S.Q. Liu, T.G. Wang, Y. Xing, Y.H. Lin and H.Q. Jia, *J. Coord. Chem*. **53**, 25 (2001).
[22] Z.H. Zhou, H.L. Wan and K.R. Tsai, *J. Chem. Soc. Dalton Trans*. 4289 (1999).
[23] C.B. Knobler, A.J. Wilson, R.N. Hider, I.W. Jensen, B.R. Penfold, W.T. Robinson and C.J. Wilkins, *J. Chem. Soc. Dalton Trans*. 1299 (1983).
[24] Z.H. Zhou, G.F. Wang, S.Y. Hou, H.L. Wan and K.R. Tsai. *Inorg. Chim. Acta* **314**, 184 (2001).
[25] L.J. Farrugia, *J. Appl. Cryst*. **32**, 837 (1999).
[26] C.K. Fair, MolEN, *An Interactive Intelligent System for Crystal Structure Analysis*. (Enraf-Nonius, Delft, The Netherland, 1990).
[27] D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, (Kynoch Press, Birmingham, UK, 1974).
[28] W.J. Geary, *Coord. Chem. Rev*. **7**, 81 (1971).
[29] W.B. Yan, S.Y. Hou, H. Zhao, Z.H. Zhou and H.L. Wan, *Huaxue Tonghao* (*Chemistry*) **64**, w117 2001.
[30] J.B. Howard and D.C. Rees, *Chem. Rev*. **96**, 2965 (1996).
[31] W.A Havere and A.T.H. Lenstra, *Bull. Soc. Chim. Belg*. **89**, 427 (1980).
[32] Z.H. Zhou, Y.J. Lin, H.B. Zhang, G.D. Lin and K.R. Tsai, *J. Coord. Chem*. **42**, 131 (1997).
[33] Z.H. Zhou, W.B. Yan, H.L. Wan and K.R. Tsai, *J. Inorg. Biochem*. **90**, 137 (2002).
[34] A.T.H. Lenstra and J. Diller, *Bull. Soc. Chim. Belg*. **92**, 257 (1983).
[35] M. Kaliva, T. Giannadaki, A. Salifoglou, C.P. Raptopoulou, A. Terzis and V. Tangoulis, *Inorg. Chem*. **40**, 3711 (2001).

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