with the terminal C atoms of their neighbouring allyl groups (max. deviation 0·05 Å), and make an angle of 82·3° to one another.

Each of the allyl groups bridges two metal atoms. The IR spectra of $[(C_3H_5Pd)_2S]_x$ indicated that all the allyl groups are μ_3-bonded to the Pd atoms (Bogdanović et al., 1983) so it would appear that during the preparation of the compound re-arrangement of the allyl groups has occurred.

Statistical disorder of the *meso* C atom in one allyl group and high standard deviations for the coordinates of the C atoms in the other unfortunately prevent a detailed discussion of geometry of the allyl groups. The Pd—Pd distance at 2·63 (1) Å (mean), however, is similar to that in other compounds containing a Pd—Pd bond bridged by an allyl group {2·686 (7), $[\mu$-C$_3$H$_5)(\mu$-I)Pd$_2$[P(C$_6$H$_5$)$_2]$ (Kobayashi, Iitaka & Yamazaki, 1972); 2·679, [(C$_5$H$_5$){2-(CH$_3$)-C$_3$H$_4$}Pd$_2$\{P(C$_6$H$_5$)$_3$\}$_2$]; 2·689, [(C$_5$H$_5$){2-(CH$_3$)C$_3$H$_4$}-Pd$_2$P(OC$_6$H$_4$-o-CH$_3$)$_3]_2$ (Werner, Kühn, Tune, Krüger, Brauer, Sekutowski & Tsay, 1977); 2·720 (1) Å, [η^3-C$_3$H$_5$PdP(C$_6$H$_5$)$_3]_2$ (Jolly, Krüger, Schick & Wilke, 1980)}.

Other bond distances and angles in the molecule are as expected. There are no intermolecular contacts between non-H atoms of less than 3·2 Å.

References

ADAMS, R. D. & FOUST, D. F. (1983). *Organometallics*, 2, 323–327.

BENN, R., BOGDANOVIĆ, B., GÖTTSCH, P. & RUBACH, M. (1983). *Z. Naturforsch. Teil B*, 38, 604–610.

BOGDANOVIĆ, B., GODDARD, R., GÖTTSCH, P., KRÜGER, C., SCHLICHTE, K. & TSAY, Y.-H. (1983). *Z. Naturforsch Teil B*, 34, 609–613.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

COLEMAN, J. M., WOJCICKI, A., POLLICK, P. J. & DAHL, L. F. (1967). *Inorg. Chem.* 6, 1236–1242.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* 18, 1035–1038.

DAVIS, R. E. & HARRIS, D. R. (1970). *DAESD.* Roswell Park Memorial Institute, USA.

DEAN, W. K. & VANDERVEER, D. G. (1978). *J. Organomet. Chem.* 146, 143–149.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JACOBSON, R. A. & LAWTON, S. L. (1965). *TRACER.* US Energy Commission, Report TID-4500. Iowa State Univ., USA.

JOHNSON, C. K. (1976). *ORTEP.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

JOLLY, P. W., KRÜGER, C., SCHICK, K. P. & WILKE, G. (1980). *Z. Naturforsch.* 35, 926–928.

KOBAYASHI, Y., IITAKA, Y. & YAMAZAKI, H. (1972). *Acta Cryst.* B28, 899–906.

LE BORGNE, G. & GRANDJEAN, D. (1975). *J. Organomet. Chem.* 92, 381–392.

ROBERTS, P. & SHELDRICK, G. M. (1976). *XANADU.* Program for crystallographic calculations. Univ. of Cambridge, England.

RUBACH, M. (1981). PhD Thesis, Ruhr-Univ. Bochum, Federal Republic of Germany.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

WERNER, H., KÜHN, A., TUNE, D. J., KRÜGER, C., BRAUER, D. J., SEKUTOWSKI, J. C. & TSAY, Y.-H. (1977). *Chem. Ber.* 110, 1763–1775.

Aquabis(pyridine-2-carboxamide oxime)copper(II) Chloride

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Abstract. $[Cu(C_6H_7N_3O)_2(H_2O)]Cl_2$, $M_r = 426.75$, monoclinic, $C2/c$, $a = 16.854$ (7), $b = 7.091$ (3), $c = 14.849$ (8) Å, $\beta = 106.39$ (4)°, $V = 1702$ (1) Å^3, $Z = 4$, $D_m = 1.66$, $D_x = 1.665$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 16.1$ cm^{-1}, $F(000) = 868.00$, room temperature, $R = 0.041$ for 1570 unique reflections. In forming the complex the oxime group of the ligand is not deprotonated. The coordination about copper(II) is distorted square pyramidal, with the bidentate ligand bound to the metal through the pyridine and oxime N atoms, the water oxygen occupying the axial position. The Cu—N(oxime), Cu—N(py) and Cu—O(w) bond lengths are 1·971 (2), 2·009 (2) and 2·284 (4) Å, respectively. The amide oxime NH$_2$ group is not used in the complexation.

Introduction. Amide oximes are versatile ligands capable of binding metal ions through the oxime N, oxime O and amide N atoms. Since the amide oxime group may or may not deprotonate upon coordination, formation of a large number of different mononuclear and polynuclear metal complexes is possible (Chakravorty, 1974).

As part of our study of the structural and equilibrium characteristics of copper(II) and

nickel(II) complexes with aminoamide oxime ligands we recently described two tetranuclear copper(II) complexes (Saarinen, Korvenranta & Orama, 1989). In both structures the coordination of copper(II) was found to involve the amide oxime group as negative R—C(NO$^-$)NH$_2$ and R—C(NO$^-$)NH$^-$ ions. In this paper we report the crystal structure of a copper(II) complex of pyridine-2-carboxamide oxime, which is mononuclear and contains undissociated —C(NOH)NH$_2$.

Experimental. Pyridine-2-carboxamide oxime ($=$HL) was prepared by reaction of hydroxylamine with 2-cyanopyridine according to the method described earlier (Saarinen, Orama, Raikas & Korvenranta, 1983). Recrystallization from hot water gave the ligand as white needles. The complex Cu(HL)$_2$-Cl$_2$.H$_2$O was obtained by evaporating an aqueous solution of HL (2 mol equiv.), CuCl$_2$ (1 mol equiv.) and NaOH (1 mol equiv.). The green block-like crystals of dimensions 0·2 × 0·3 × 0·4 mm used in the analysis were obtained by recrystallization from water. D_m by flotation. A Nicolet $P3$ four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used. The cell parameters were determined from 20 reflections, $5·0 < 2\theta < 24·0°$. The intensities of 2277 ($-22 \le h \le 22$, $0 \le k \le 9$, $0 \le l \le 20$) independent reflections were measured with $2\theta < 58·0°$, of which 1570 with $I > 3\sigma(I)$ were used in the least-squares refinement. Three standard reflections were checked every 58 reflections. No significant deviations were observed. An empirical absorption correction was based on ψ-scan data (eight reflections, transmission range 0·64–1·00). The structure was solved by the heavy-atom technique with $SHELX86$ (Sheldrick, 1985) (atoms from difference synthesis) and refined by least squares with aniso-tropic non-H atoms ($SHELX76$, Sheldrick, 1976) using F; the H atoms were refined with isotropic temperature factors; $w = (\sigma^2 + 0·0062F^2)^{-1}$, $R = 0·041$, $wR = 0·045$ for 1570 reflections. Final $(\Delta/\sigma)_{max} = 0·13$, $S = 0·82$, max. and min. heights in final difference synthesis 0·55 and $-0·68$ e Å^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). PLUTO78 (Motherwell & Clegg, 1978) was used for the diagrams.

Discussion. The atomic parameters are given in Table 1, and the bond distances and angles in Table 2.* A view of the complex cation and the numbering

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^2$) *for the non-H atoms*

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

	x	y	z	U_{eq}
Cu	0	2465·9 (7)	2500	3·47 (3)
Cl	−3460·9 (5)	2003·2 (14)	3591·0 (6)	4·89 (5)
O1	1785 (1)	3450 (4)	2575 (2)	4·76 (12)
O2	0	−705 (5)	2500	6·01 (22)
N1	−512 (2)	2288 (3)	1107 (2)	3·49 (11)
N2	961 (2)	3102 (4)	2050 (2)	3·92 (12)
N3	1483 (2)	3265 (5)	767 (2)	4·46 (14)
C1	875 (2)	3014 (4)	1159 (2)	3·30 (12)
C2	17 (2)	2575 (4)	590 (2)	3·26 (12)
C3	−228 (2)	2423 (4)	−380 (2)	4·03 (14)
C4	−1044 (2)	1897 (5)	−824 (2)	4·59 (16)
C5	−1569 (2)	1533 (5)	−292 (2)	4·39 (15)
C6	−1289 (2)	1744 (5)	669 (2)	4·05 (14)

Table 2. *Bond lengths* (Å) *and angles* (°)

Cu—N1	2·009 (3)	N3—C1	1·325 (5)
Cu—N2	1·971 (3)	C1—C2	1·488 (4)
Cu—O2	2·248 (4)	C2—C3	1·385 (4)
N2—O1	1·410 (3)	C3—C4	1·398 (4)
N1—C2	1·346 (4)	C4—C5	1·366 (5)
N1—C6	1·344 (4)	C5—C6	1·379 (4)
N2—C1	1·290 (4)		
N1—Cu—N2	79·6 (1)	O1—N2—C1	112·5 (3)
N1—Cu—O2	86·4 (1)	N2—C1—N3	124·6 (3)
N2—Cu—O2	103·2 (1)	N2—C1—C2	113·7 (3)
N1—Cu—N1*	172·8 (1)	N3—C1—C2	121·8 (3)
N1—Cu—N2*	102·1 (1)	N1—C2—C1	113·7 (3)
N2—Cu—N2*	153·5 (1)	N1—C2—C3	122·0 (3)
Cu—N1—C2	114·6 (2)	C1—C2—C3	124·3 (3)
Cu—N1—C6	126·3 (2)	C2—C3—C4	118·4 (3)
C2—N1—C6	118·7 (3)	C3—C4—C5	119·2 (3)
Cu—N2—O1	128·9 (2)	C4—C5—C6	119·4 (3)
Cu—N2—C1	118·2 (2)	C5—C6—N1	122·2 (3)

* Atom in position $-x, y, -z + \tfrac{1}{2}$.

scheme are shown in Fig. 1. A stereoscopic view of the packing is presented in Fig. 2.

The coordination environment of the Cu^{II} atom is roughly square-pyramidal and there is a marked tetrahedral distortion of the CuN$_4$ basal plane: the deviation of the basal N atoms from their least-squares plane is 0·289 (4) Å and the dihedral angle between the planes CuN1N2 and CuN1'N2' is 32·1 (1)° (cf. Fig. 2).

The amide oxime NH$_2$ group is not used in the complexation: instead the preferred binding sites are the N(oxime) and N(py) atoms. This is in agreement with the common observation that the NH$_2$ function exhibits only a slight affinity for metal coordination when it is conjugated to an unsaturated system (Stout, Sundaralingam & Lin, 1972).

The presence of the NH$_2$ group in the ligand is not, however, without consequence for the complex geometry. The delocalization of the lone electron pair formally on the amide N produces a marked increase in the electron density on the oxime N atom,

with the result that the thermodynamic stability of amide oxime $Cu(HL)_n^{2+}$ complexes is considerably higher than that of oxime structures containing an H atom or an alkyl group in place of the NH_2 group (Saarinen, Orama, Raikas & Korvenranta, 1986).

The stronger metal–ligand interactions associated with the amide group should appear in a shortening of the M—N(oxime) distance and lengthening of the N—O distance. Such changes are clearly observed in the octahedral oxime complexes of nickel(II) (Saarinen, Korvenranta, Orama & Raikas, 1984), but in the corresponding copper(II) complexes the coordination about the metal is more flexible and direct comparison of the bond distances between different types of structures is not always possible.

The Cu—N(oxime) and N—O bond lengths of the accurately known 5- and 4 + 2-coordinate structures containing undissociated oxime groups are given in Table 3. Although the values presumably reflect the variations in the geometrical and steric requirements of the different ligands, the N—O distances turn out to be consistently longer and most of the Cu—N(oxime) distances somewhat shorter in the amide oxime structures than in the other compounds.

Most of the reported copper(II) complexes with oxime ligands are polynuclear containing oximato

Fig. 1. Perspective view of the complex cation.

Fig. 2. Stereoscopic view of the unit cell.

Table 3. *Comparison of the* Cu—N(*oxime*) *and* N—O(H) *bond distances* (Å) *in different copper–oxime complexes*

	Cu—N(oxime)	N—O(H)	Reference
Amidoxime ligands			
$[Cu(HL)_2Cl]^a$	1·971 (2)	1·410 (3)	This work
$[Cu(H_2L)_2(NO_3)_2]^b$	1·966 (5)	1·400 (6)	Endres & Genc (1983)
	1·979 (5)	1·405 (6)	
$[Cu(HL)(H_2O)(SO_4)].3H_2O^c$	1·960 (2)	1·412 (3)	Sletten, Marthinsen & Sletten (1985)
$[Cu(HL)_2](ClO_4)_2^c$	1·968 (4)	1·420 (5)	Stout et al. (1972)
$[Cu(H_2L)_2]Cl_2^d$	1·959 (3)	1·403 (5)	Cullen & Lingafelter (1970)
	1·951 (3)	1·417 (4)	
	1·976 (3)	1·422 (3)	
$[Cu(H_2L)Cl_2]^b$	1·971 (20)	1·409 (22)	Endres, Genc & Nöthe (1983)
	1·927 (19)	1·417 (22)	
$[Cu(H_2L)(HL)Cl]^b$	2·000 (3)	1·405 (3)	Endres, Genc & Nöthe (1983)
	1·988 (3)	1·414 (3)	
$[Cu(H_2L)Cl_2]^b$	1·937 (8)	1·420 (12)	Endres (1983)
	1·981 (12)	1·413 (13)	
Other ligands			
$[Cu(HL)_2](BF_4)_2.2H_2O^e$	2·064 (4)	1·387 (7)	Nicholson, Petersen & McCormick (1980)
	2·081 (4)	1·396 (6)	
$[Cu(H_2L)Cl_2]^f$	1·991 (7)	1·366 (7)	Mégnamisi-Bélombé, Singh, Bolster & Hatfield (1984)
$[Cu(H_2L)Br_2]^f$	1·987 (5)	1·365 (6)	Endres, Andoseh & Mégnamisi-Bélombé (1981)
	2·007 (5)	1·367 (6)	
$[Cu(H_2L)Br_2]^g$	1·990 (7)	1·380 (12)	Mégnamisi-Bélombé & Endres (1983a)
	2·000 (8)	1·379 (4)	
$[Cu_2(H_2L)_2Cl_4]^g$	1·998 (2)	1·386 (4)	Mégnamisi-Bélombé & Endres (1983b)
	2·016 (3)	1·379 (4)	
$[Cu_2(H_2L)_2Br_2]^h$	2·014 (6)	1·385 (8)	Endres (1978)
	1·994 (6)	1·408 (8)	

Notes: (a) HL = pyridine-2-carboxamide oxime, (b) H_2L = oxamide oxime, (c) HL = 4-aminoimidazole-5-carboxamide oxime, (d) H_2L = 2,2'-iminobis-(acetamide oxime), (e) H_2L = 2,6-diacetylpyridine dioxime, (f) H_2L = diphenylethanedione dioxime, (g) H_2L = 1,2-cyclohexanedione dioxime, (h) H_2L = 2,3-butanedione dioxime.
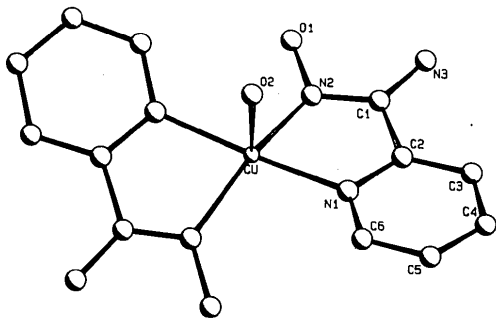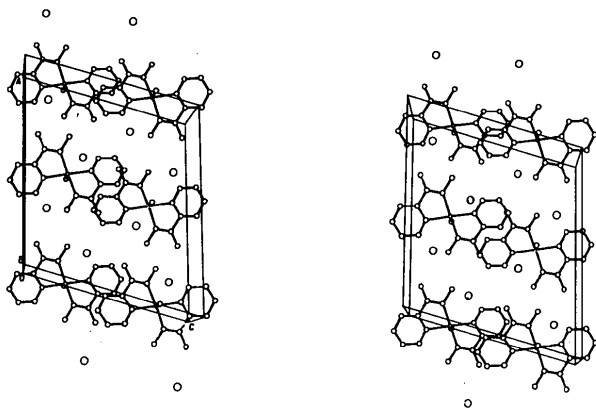
NO groups between Cu atoms. One such structure is the trinuclear oximato complex that readily forms with pyridine-2-aldoxime (Beckett & Hoskins, 1972). An apparent reason for the different nature of the title compound is the weakened acidity of the coordinated NOH groups owing to the presence of the amide NH_2 group in the ligand molecule. Thus more alkaline conditions than those used here in the complex preparation would be needed to promote oxime deprotonation and subsequent polymerization.

References

BECKETT, R. & HOSKINS, B. F. (1972). *J. Chem. Soc. Dalton Trans.* pp. 291–295.

CHAKRAVORTY, A. (1974). *Coord. Chem. Rev.* **13**, 1–43.

CULLEN, D. L. & LINGAFELTER, A. C. (1970). *Inorg. Chem.* **9**, 1865–1877.

ENDRES, H. (1978). *Acta Cryst.* **B34**, 3736–3739.

ENDRES, H. (1983). *Acta Cryst.* **C39**, 1192–1194.

ENDRES, H., ANDOSEH, I. N. & MÉGNAMISI-BÉLOMBÉ, M. (1981). *Acta Cryst.* **B37**, 681–683.

ENDRES, H. & GENC, N. (1983). *Acta Cryst.* **C39**, 704–705.

ENDRES, H., GENC, N. & NÖTHE, D. (1983). *Z. Naturforsch. Teil B*, **38**, 90–95.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MÉGNAMISI-BÉLOMBÉ, M. & ENDRES, H. (1983a). *Acta Cryst.* **C39**, 707–709.

MÉGNAMISI-BÉLOMBÉ, M. & ENDRES, H. (1983b). Acta Cryst. C39, 1190–1192.

MÉGNAMISI-BÉLOMBÉ, M., SINGH, P., BOLSTER, D. E. & HATFIELD, W. E. (1984). Inorg. Chem. 23, 2578–2582.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NICHOLSON, G. A., PETERSEN, J. L. & McCORMICK, B. J. (1980). Inorg. Chem. 19, 195–200.

SAARINEN, H., KORVENRANTA, J. & ORAMA, M. (1989). Acta Chem. Scand. Ser. A. In the press.

SAARINEN, H., KORVENRANTA, J., ORAMA, M. & RAIKAS, T. (1984). Acta Chem. Scand. Ser. A, 38, 265–275.

SAARINEN, H., ORAMA, M., RAIKAS, T. & KORVENRANTA, J. (1983). Acta Chem. Scand. Ser. A, 37, 631–636.

SAARINEN, H., ORAMA, M., RAIKAS, T. & KORVENRANTA, J. (1986). Acta Chem. Scand. Ser. A, 40, 396–401.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). Crystallographic Computing 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

SLETTEN, E., MARTHINSEN, T. & SLETTEN, J. (1985). Inorg. Chim. Acta, 106, 1–6.

STOUT, C. D., SUNDARALINGAM, M. & LIN, G. H.-Y. (1972). Acta Cryst. B28, 2136–2141.

Structural Characterization of the Manganese(IV) Schiff-Base Complex Mn^{IV}(5-Cl-SALAHP)$_2$

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Abstract. Bis[3-(5-chlorosalicylideneamino)propanolato-O,N,O']manganese(IV) methanol solvate, [Mn(C$_{10}$H$_{10}$ClNO$_2$)$_2$].CH$_3$OH, M_r = 510·3, monoclinic, $P2_1/c$, a = 11·949 (2), b = 7·530 (2), c = 25·777 (6) Å, β = 105·75 (2)°, V = 2232·4 (8) Å^3, Z = 4, D_x = 1·518 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 7·98 cm^{-1}, F(000) = 1502, T = 300 K, R = 0·0343, wR = 0·032 for 2113 unique reflections with $(I) > 3\sigma(I)$. The title complex Mn^{IV}(5-Cl-SALAHP)$_2$ [5-Cl-SALAHP = 3-(5-chlorosalicylideneamino)propanolato] displays a regular octahedral geometry. The 5-Cl-SALAHP ligand is tridentate, forming a meridional chelate with one phenolato oxygen (Mn—O$_{avg}$ = 1·90 Å), one alkoxide oxygen (Mn—O$_{avg}$ = 1·85 Å) and one imine nitrogen (Mn—N$_{avg}$ = 2·02 Å) coordinated to the metal. Important angles described by the six atoms bound to manganese are all very close to either 180 or 90° except the N—Mn—N angle which is 174·7°. Previous studies have shown that Mn^{IV}(5-Cl-SALAHP)$_2$ displays a rhombic EPR spectrum with well-resolved ^{55}Mn hyperfine structure on g_x, g_y and g_z. In contrast, Mn(SALADHP)$_2$ [SALADHP = 2-methyl-2-(salicylideneamino)-1,3-propanediolato] shows a broad, ill-defined signal at g = 5·15 and a weak g = 2 component. The different spectral forms result from the extent of distortion of the Mn^{IV} octahedron. The reported structure is of potential importance to the understanding of the photosynthetic water-oxidizing system.

Introduction. Elucidation of the structure of the metallocenter of the photosynthetic oxygen-evolving complex (OEC) has garnered considerable interest in recent years. The Mn^{IV} oxidation level has been invoked as an intermediate in nearly every model that has been proposed for this enzymic reaction (Pecoraro, 1988; Babcock, 1987). The EPR spectral features in the S_2 oxidation level of the OEC have fueled considerable debate regarding the core structure and metal oxidation states of the manganese (de Paula, Beck & Brudvig, 1986; Hansson, Aasa & Vanngard, 1987). Both a g = 2 multiline (Dismukes & Siderer, 1980) and a g = 4·1 derivative signal have been observed using the spinach enzyme (Casey & Sauer, 1984). A tetranuclear model that invoked a conformational change for the origin of the two signals was initially proposed (de Paula, Beck & Brudvig, 1986); however, a new interpretation assigns the g = 2 multiline signal to a mixed-valence dimer and the g = 4 signal to a mononuclear Mn^{IV} (Hansson, Aasa & Vanngard, 1987). A mononuclear/trinuclear formulation has also been put forward (Pecoraro, 1988). Recently, it was noted that the g = 4 signal could not be generated from photosynthetic membranes of the cyanobacterium *Synechococcus* (McDermott, Yachandra, Guiles, Cole, Dexheimer, Britt, Sauer & Klein, 1988). These authors suggested that the different behavior of the spinach and *Synechoccous* enzymes may be due to changes in the zero-field splitting parameters of Mn^{IV}. Unfortunately, there are very few structurally characterized Mn^{IV} complexes with reported EPR spectra.