ELSEVIER

Inorganica Chimica Acta 340 (2002) 65–69

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis and reactions of platinum(IV) complexes with sodium ascorbate

Malcolm J. Arendse [a], Gordon K. Anderson [b,*], Raquel N. Majola [a], Nigam P. Rath [b]

[a] *Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa*
[b] *Department of Chemistry, University of Missouri–St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121, USA*

Received 7 January 2002; accepted 3 May 2002

Abstract

The platinum(IV) complexes $[PtCl_2(OH)_2(N^{\frown}N)]$ ($N^{\frown}N$ = en, *N*,*N*-dmen, *N*,*N*′-dmen) were prepared by oxidation of $[PtCl_2(N^{\frown}N)]$ with hydrogen peroxide. The complexes were characterized by multinuclear NMR and infrared spectroscopy, as well as microanalysis. The reactions of these compounds with sodium ascorbate were monitored spectroscopically. Reduction of the platinum(IV) complexes by sodium ascorbate occurred only slowly. An oxalatoplatinum(IV) complex $[Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})]\cdot H_2O$ was isolated from the reaction of $[PtCl_2(OH)_2(N,N\text{-dmen})]$ and sodium ascorbate and characterized by an X-ray diffraction study.

Keywords: Platinum complexes; Antitumor activity; Ascorbic acid; Oxalate; Oxidation

1. Introduction

Platinum(IV) complexes, such as iproplatin, $[PtCl_2(OH)_2(NH_2Pr^i)_2]$, are currently used as antitumor drugs in chemotherapy, where their higher water solubility makes oral administration possible. These platinum(IV) compounds have less severe side effects than cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, and they are active against certain tumor cells that are resistant to cisplatin [1–4]. Platinum(IV) complexes generally undergo ligand substitution more slowly than their platinum(II) analogues [5] and, since platinum(II) species are known to bind to DNA, it is believed that platinum(IV) complexes serve as prodrugs for platinum(II) derivatives. Thus, they must be reduced in vivo before DNA binding occurs. A number of cellular reductants could achieve this, including cysteine, the sulfhydryl protein, glutathione and ascorbic acid.

A recent study focused on the reduction of platinum(IV) complexes by ascorbic acid. Choi and coworkers found that the rate of reduction of $[PtX_2Cl_2L_2]$ (X = OH, Cl, $OCOCH_3$, $OCOCF_3$; L_2 = en, dach or L = NH_2Pr^i) was dependent on the nature of the axial ligands and the amine ligands [6]. For the ethylenediamine complexes, the reduction rates and reduction potentials were found to increase in the order OH < $OCOCH_3$ < Cl < $OCOCF_3$, which follows the order of increasing electron-withdrawing abilities of the ligands. Reduction of the ethylenediamine complexes was slower than the corresponding reactions of the diaminocyclohexane or isopropylamine complexes. Hambley and coworkers earlier investigated the electrochemical reduction of platinum(IV) complexes $[Pt(en)Cl_2Y_2]$ (Y = Cl, OH, RCOO) and found that the tetrachloro complexes were reduced more readily than the complexes with hydroxo or carboxylato axial ligands [7]. We have investigated the effect of N-methyl substituents on the rate of ascorbic acid reduction of ethylenediamineplatinum(IV) complexes, and the results of this study are presented here.

2. Experimental

K_2PtCl_4, deuterium oxide, *N*,*N*-dmen and *N*,*N*′-dmen were purchased from Sigma Aldrich. $[PtI_2(N,N\text{-}$

* Corresponding author. Tel.: +1-314-516-5311; fax: +1-314-516-5342
E-mail address: ganderson@umsl.edu (G.K. Anderson).

0020-1693/02/$ - see front matter
PII: S0020-1693(02)01058-7

dmen)] and [PtI_2(*N*,*N*′-dmen)] were prepared as described elsewhere [8]. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer as nujol mulls. UV–Vis spectra were recorded on a GBC UV–Vis 920 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. Chemical shifts were referenced relative to D_2O at 4.80 ppm. ^{195}Pt{^{1}H} NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. Chemical shifts were referenced to an external sample of K_2PtCl_4 at −1624 ppm relative to H_2PtCl_6 at 0 ppm. Microanalyses were performed by Atlantic Microlab, Norcross, GA.

2.1. Crystallographic measurements and structure resolution

Crystallographic measurements were performed on a Bruker SMART CCD detector system single crystal X-ray diffractometer at a temperature of 213(2) K as described elsewhere [9]. Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package [10].

2.2. Preparation of [$PtCl_2$(*N*^*N*)]

[PtI_2(*N*^*N*)] (1.1 g, 2.0 mmol) was suspended in water (40 ml). Silver nitrate (0.68 g, 4.0 mmol) in H_2O (6 ml) was then added to the [PtI_2(*N*^*N*)] suspension. The reaction mixture was then stirred for 2 h at 50 °C in a flask protected from light. After this time the precipitate of AgI was removed by filtration. The filtrate was collected and excess NaCl (1.2 g, 20 mmol) in H_2O (6 ml) was added to the filtrate. The reaction mixture was allowed to stir for 30 min at 50 °C. The yellow solution was then cooled in the refrigerator for 2 days and yellow crystals were obtained.

[$PtCl_2$(*N*,*N*-dmen)]: yield 0.25 g, 69%. *Anal.* Calc. for $C_4H_{12}Cl_2N_2Pt$: C, 13.56; H, 3.39; N, 7.91. Found: C, 13.59; H, 3.37; N, 7.89%. ^{1}H NMR (D_2O) δ 2.89 (s, $^3J_{PtH}$ = 30 Hz, 6H, CH_3); 2.70 (s, 4H, CH_2).

[$PtCl_2$(*N*,*N*′-dmen)]: yield 0.26 g, 72%. *Anal.* Calc. for $C_4H_{12}Cl_2N_2Pt$: C, 13.56; H, 3.39; N, 7.91. Found: C, 13.62; H, 3.49; N, 7.78%. ^{1}H NMR (D_2O) δ 2.66 (s, $^3J_{PtH}$ = 42 Hz, 6H, CH_3); 2.88 (s, 4H, CH_2).

2.3. Preparation of [$PtCl_2(OH)_2$(*N*^*N*)]

A solution of [$PtCl_2$(*N*^*N*)] (0.18 g, 0.50 mmol) in water (10 ml) was treated with a tenfold excess of 3% H_2O_2 (11 ml) at 50 °C for 2 h. The solvent was removed under reduced pressure and the product was collected as a yellow solid, which was washed with ether and dried in vacuo.

[$PtCl_2(OH)_2$(*N*,*N*-dmen)]: yield 0.16 g, 82%. *Anal.* Calc. for $C_4H_{16}Cl_2N_2O_2Pt$: C, 12.37; H, 3.61; N, 7.22. Found: C, 12.30; H, 3.66; N, 6.69%. ^{1}H NMR (D_2O): δ 2.76 (s, $^3J_{PtH}$ = 26 Hz, 6H, CH_3), 2.95 (dd, $^3J_{HH}$ = 12, 3 Hz, 2H, CH_2), 3.02 (dd, $^3J_{HH}$ = 12, 3 Hz, 2H, CH_2). ^{195}Pt{^{1}H} NMR: δ 770 (s).

[$PtCl_2(OH)_2$(*N*,*N*′-dmen)]: yield 0.17 g, 87%. *Anal.* Calc. for $C_4H_{16}Cl_2N_2O_2Pt$: C, 12.37; H, 3.61; N, 7.22. Found: C, 11.81; H, 3.38; N, 6.73%. ^{1}H NMR (D_2O): δ 2.59 (s, $^3J_{PtH}$ = 32 Hz, 6H, CH_3), 2.85 (s, 4H, CH_2). ^{195}Pt{^{1}H} NMR: δ 782 (s).

2.4. Reactions of [$PtCl_2(OH)_2$(*N*,*N*-dmen)] with sodium ascorbate

A solution of [$PtCl_2(OH)_2$(*N*,*N*-dmen)] (0.029 g, 0.075 mmol) and sodium ascorbate (0.15 g, 0.75 mmol) in D_2O (2.0 ml) was allowed to stir at ambient temperature for 48 h. Yellow crystals, which were suitable for an X-ray diffraction study, separated on standing.

2.5. Reactions of [$PtCl_2(OH)_2$(*N*,*N*-dmen)] with sodium oxalate

[$PtCl_2(OH)_2$(*N*,*N*-dmen)] (0.10 g, 0.25 mmol) was dissolved in water (10 ml) and sodium oxalate (0.04 g, 0.25 mmol) was added to the solution. The reaction mixture was then allowed to stir at room temperature for 72 h and monitored by ^{1}H NMR spectroscopy.

2.6. Reactions of [$PtCl_2(OH)_2$(*N*,*N*-dmen)] with sodium oxalate in presence of platinum(II)

[$PtCl_2(OH)_2$(*N*,*N*-dmen)] (0.01 g, 0.025 mmol) and sodium oxalate (0.004 g, 0.025 mmol) were dissolved in D_2O (0.5 ml). [$PtCl_2$(*N*,*N*-dmen)] (0.001 g, 0.0025 mmol) was added to the solution and the reaction mixture was allowed to stir at room temperature for 7 days. ^{1}H NMR spectra of the solution were recorded periodically.

2.7. Reaction of [$PtCl_2(OH)_2$(*N*,*N*-dmen)] with oxalic acid

[$PtCl_2(OH)_2$(*N*,*N*-dmen)] (0.11 g, 0.28 mmol) was dissolved in water (10 ml) and oxalic acid (0.061 g, 0.50 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 4 days in a flask protected from light. A pale yellow precipitate was obtained and the precipitate was collected by filtration. A pale yellow solid was obtained.

3. Results and discussion

3.1. Preparation of platinum(IV) complexes

Platinum(IV) complexes containing diamine ligands may be prepared by oxidation of the corresponding platinum(II) precursors using hydrogen peroxide or chlorine. The platinum(II) complexes $[PtCl_2(N^{\frown}N)]$ ($N^{\frown}N$ = en, *N*,*N*-dmen, *N*,*N*′-dmen) were prepared in good yields by reaction of $[PtI_2(N^{\frown}N)]$ with 2 equiv. of $AgNO_3$ in aqueous solution [7,11], followed by addition of excess sodium chloride. Further treatment with excess hydrogen peroxide in water at 50 °C for 1 h gave the platinum(IV) derivatives, $[PtCl_2(OH)_2(N^{\frown}N)]$.

The ^{1}H NMR spectrum of $[PtCl_2(N,N\text{-dmen})]$ exhibits a singlet resonance at 2.89 ppm with ^{195}Pt satellites ($^3J_{PtH} = 36$ Hz) due to the N-methyl groups, and a broad resonance at 2.70 ppm due to the nonequivalent CH_2 hydrogens of the ligand backbone. Upon oxidation to $[PtCl_2(OH)_2(N,N\text{-dmen})]$, the N-methyl signal shifts slightly to lower frequency (2.76 ppm), and the coupling to ^{195}Pt is reduced to 26 Hz as expected when the complex geometry changes from square planar to octahedral. The methylene hydrogens give rise to complex multiplets at 2.98 and 3.02 ppm. The ^{1}H NMR spectrum of $[PtCl_2(N,N'\text{-dmen})]$ exhibits a singlet resonance at 2.66 ppm with ^{195}Pt satellites ($^3J_{PtH} = 42$ Hz) due to the protons of the N-methyl groups, and a singlet at 2.88 ppm due to the methylene hydrogens of the ligand backbone. In the ^{1}H NMR spectrum of $[PtCl_2(OH)_2(N,N'\text{-dmen})]$, the N-methyl resonance occurs at lower frequency (2.59 ppm) and the coupling to ^{195}Pt is reduced to 30 Hz. The methylene protons give rise to a singlet at 2.85 ppm. The ^{195}Pt NMR spectra of $[PtCl_2(OH)_2(N,N\text{-dmen})]$ and $[PtCl_2(OH)_2(N,N'\text{-dmen})]$ exhibit signals at 770 and 782 ppm, respectively. These chemical shifts are typical of platinum(IV) complexes containing diamine ligands [1,2].

3.2. Reactions of platinum(IV) complexes

Reactions of $[PtCl_2(OH)_2(N^{\frown}N)]$ ($N^{\frown}N$ = en, *N*,*N*-dmen, *N*,*N*′-dmen) with a 10-fold excess of ascorbic acid in aqueous solution at pH 7 were monitored by UV–Vis spectroscopy. The platinum(IV) complexes exhibit strong absorptions between 330 and 350 nm, and these should disappear when the complexes are reduced [6]. The spectra showed no detectable change over 2 h, however, indicating that the complexes were not reduced rapidly under these conditions. In order to gain some insight into what might take place during these reactions, $[PtCl_2(OH)_2(N,N\text{-dmen})]$ was treated with sodium ascorbate in D_2O and the reaction was monitored by ^{1}H NMR spectroscopy over 48 h. In the early stages of the reaction only signals due to the reactants could be observed, but after 24 h resonances due to $[PtCl_2(N,N\text{-dmen})]$ and dehydroascorbic acid (4.20, 4.29 and 4.61 ppm) were detectable. In addition, low intensity signals were observed at 3.75 (m), 4.03 (dt, $^3J_{HH} = 6$, 2 Hz), and 4.53 ppm (d, $^3J_{HH} = 2$ Hz), which could be due to a platinum(IV) ascorbate complex. When the solution was allowed to stand for an extended period of time, yellow crystals of the oxalatoplatinum(IV) complex $[Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})].H_2O$ separated.

3.3. Crystal structure of $Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})]\cdot H_2O$

Crystal data for $[Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})]\cdot H_2O$ and refinement parameters are listed in Table 1. The complex crystallized in the centrosymmetric space group $P2_1/n$. Its molecular structure is shown in Fig. 1. It is the first example of a neutral platinum(IV) oxalate complex to be characterized crystallographically (vide infra). The complex consists of a platinum atom coordinated by a distorted octahedral array of bidentate oxalate and *N*,*N*-dmen ligands, one chloride and one hydroxide. The chloride and hydroxide are mutually *cis*, the former lying *trans* to the unsubstituted nitrogen of the diamine, and the hydroxide *trans* to one arm of the oxalate. The complex exists as two enantiomers, both of which are present in the solid state structure. Selected bond distances and angles are listed in Table 2. The Pt–O bond distances involving the oxalate ligands are essentially identical, being about 0.03 Å longer than the Pt–OH distance. The Pt–OH distance of 1.987(4) Å is similar to those observed in other hydroxoplatinum(IV) complexes containing diamine ligands [12,13]. The Pt–N bond *trans* to Cl (2.065(5) Å) is slightly longer than that *trans* to oxalate (2.034(5) Å), reflecting the higher *trans*-influence of chloride. The mean Pt–N distance (2.050 Å)

Table 1
Crystal data and structure refinement parameters for $[Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})]\cdot H_2O$

Formula	$C_6H_{15}ClN_2O_6Pt$
M_w	441.74
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.0205(8)
b (Å)	11.9868(13)
c (Å)	13.6133(15)
β (°)	98.335(4)
V (Å^3)	1133.5(2)
Z	4
ρ_{calc} (g cm^{-3})	2.589
μ(Mo Kα) (mm^{-1})	12.630
F(000)	832
R_1 ($F > 2\sigma$)	0.0266
wR_2 (all data)	0.0678
R_{int}	0.026

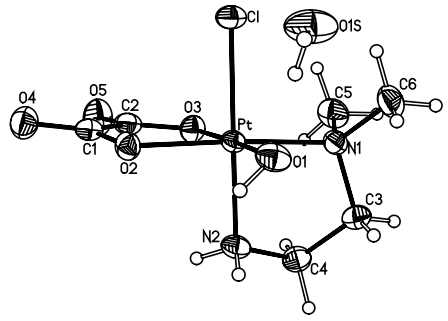

Fig. 1. Molecular structure of $[Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})]\cdot H_2O$ showing the atom-numbering scheme.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Pt(C_2O_4)(OH)Cl(N,N\text{-dmen})]\cdot H_2O$

Bond lengths			
Pt–O(1)	1.987(4)	O(3)–C(2)	1.298(7)
Pt–O(2)	2.018(4)	O(4)–C(1)	1.226(7)
Pt–O(3)	2.022(4)	O(5)–C(2)	1.224(7)
Pt–N(1)	2.065(5)	C(1)–C(2)	1.532(8)
Pt–N(2)	2.034(4)	N(1)–C(3)	1.497(7)
Pt–C(l)	2.3151(13)	N(1)–C(5)	1.496(8)
O(2)–C(1)	1.283(7)	N(2)–C(4)	1.494(8)
Bond angles			
O(1)–Pt–O(2)	93.81(17)	O(2)–Pt–N(1)	176.47(16)
O(1)–Pt–O(3)	176.49(16)	O(3)–Pt–N(1)	95.60(18)
O(2)–Pt–O(3)	82.72(15)	N(2)–Pt–N(1)	85.07(19)
O(1)–Pt–N(2)	90.86(17)	O(1)–Pt–Cl	91.19(11)
O(2)–Pt–N(2)	91.77(18)	O(2)–Pt–Cl	89.16(11)
O(3)–Pt–N(2)	88.67(16)	O(3)–Pt–Cl	89.34(11)
O(1)–Pt–N(1)	87.83(18)	N(1)–Pt–Cl	93.94(13)

is within the normal range observed for diamineplatinum(IV) complexes [12,13]. The bond angles about platinum range from 82.72 to 93.94°. The smallest angles are those associated with the two 5-membered rings (O–Pt–O = 82.72(15)°; N–Pt–N = 85.07(19)°), and the largest (95.60(18)°) is that between O3 and N1, the bulky $N(CH_3)_2$ group. The bis(oxalato)-platinum(IV) dianions *trans*-$[Pt(C_2O_4)_2X_2]^{2-}$ (X = Cl, Br, I, OH) have also been characterized by X-ray diffraction [14,15]. In these, the Pt–O distances range from 1.99 to 2.02 Å, the chloro complex, for example, exhibiting bonds that span this range of distances. In $[Pt(C_2O_4)_2(OH)_2]^{2-}$ the Pt–OH distances are 1.992(7) Å [12], identical to that in the present complex.

3.4. Formation of oxalatoplatinum(IV) complexes

We have shown that platinum(II) ascorbate complexes may be oxidized in air to give the corresponding oxalates [16]. Formation of the platinum(IV) oxalate $[Pt(C_2O_4)Cl(OH)(N,N\text{-dmen})]$ was surprising, however, because reduction of platinum(IV) was expected to accompany oxidation of the ascorbate ligand. Its formation might suggest that oxidative degradation of the ascorbate complex had occurred without reduction of platinum(IV), although other mechanisms may be envisaged.

The reaction of $[PtCl_2(OH)_2(N,N\text{-dmen})]$ with sodium ascorbate is likely to proceed by initial displacement of one of the axial hydroxo groups by ascorbate. Such monodentate ascorbate complexes have been proposed previously as intermediates in the reduction of platinum(IV) complexes [17]. At this stage intramolecular degradation of ascorbate could take place. Alternatively, oxidation of the ascorbate ligand could produce the observed dehydroascorbic acid and water, simultaneously generating the platinum(II) complex $[PtCl_2(N,N\text{-dmen})]$. Dehydroascorbic acid is known to react slowly to form oxalic and threonic acids [18,19], and reaction of the platinum(IV) precursor with the oxalic acid thus produced could generate the isolated product. In any case, reaction of $[PtCl_2(OH)_2(N,N\text{-dmen})]$ with sodium ascorbate is either very slow or involves an unfavorable equilibrium, such that the platinum(IV) complex dominates the NMR spectra. Only after an extended period of time was the oxalatoplatinum(IV) complex formed, and then only in low yield.

We investigated the reaction of $[PtCl_2(OH)_2(N,N\text{-dmen})]$ with sodium oxalate, as well as with oxalic acid, to try to establish how the oxalatoplatinum(IV) complex may be produced. ^1H NMR studies of the reaction between $[PtCl_2(OH)_2(N,N\text{-dmen})]$ and $Na_2C_2O_4$ suggested that no reaction had occurred after 4 days. The ^1H NMR spectrum of the reaction mixture indicated the presence of the starting material only. Similarly, no change was observed in the ^1H NMR spectrum of the reaction between $[PtCl_2(OH)_2(N,N\text{-dmen})]$ and excess oxalic acid after monitoring for 4 days (although an unidentified pale yellow solid precipitated from the reaction mixture).

In order to establish whether the presence of a platinum(II) complex might accelerate the production of the oxalatoplatinum(IV) complex, we monitored the reaction between $[PtCl_2(OH)_2(N,N\text{-dmen})]$ and sodium oxalate in the presence of a catalytic amount of $[PtCl_2(N,N\text{-dmen})]$ by ^1H NMR spectroscopy. It has been shown that substitution reactions of platinum(IV) complexes can be accelerated by the presence of platinum(II) species that promote ligand substitution through the formation of bridged platinum(II)-platinum(IV) intermediates [20]. However, in this case the only effect seemed to be to produce more of the platinum(II) complex.

Since direct addition of oxalate (or oxalic acid) to $[PtCl_2(OH)_2(N,N\text{-dmen})]$, with or without added platinum(II) complex, does not appear to give oxalatoplatinum(IV) derivatives, it may be that the latter are indeed

formed in the reaction of $[PtCl_2(OH)_2(N,N\text{-dmen})]$ with ascorbate by intramolecular degradation of coordinated ascorbate.

4. Conclusions

Synthesis of the complexes $[PtCl_2(OH)_2(N^{\frown}N)]$ by oxidation of $[PtCl_2(N^{\frown}N)]$ with aqueous H_2O_2 was achieved in high yields ($>80\%$). Reduction of the platinum(IV) complexes to platinum(II) by sodium ascorbate appears to be slow. The reactions between $[PtCl_2(OH)_2(N^{\frown}N)]$ and sodium oxalate or oxalic acid did not produce oxalatoplatinum(IV) species, whereas the addition of a catalytic amount of $[PtCl_2(N^{\frown}N)]$ appeared to enhance the rate of reduction of platinum-(IV) to platinum(II).

5. Supplementary material

Tables of bond lengths and angles (S1), anisotropic displacement parameters (S2), and hydrogen atom coordinates and isotropic displacement parameters (S3) are available from the authors upon request.

Acknowledgements

This work was supported through a grant from the National Science Foundation (grant number CHE-9508228), a University of Missouri–St. Louis Research Award and a grant from the University of the Western Cape Linkage Program. Thanks are expressed to NSF for grants for the purchase of NMR and X-ray instrumentation.

References

[1] A.R. Khokhar, Y. Deng, Y. Kido, Z.H. Siddik, J. Inorg. Biochem. 50 (1993) 79.
[2] A.R. Khokhar, Y. Deng, S. Al-Baker, M. Yoshida, Z.H. Siddik, J. Inorg. Biochem. 51 (1993) 677.
[3] L.R. Kelland, B.A. Murrer, G. Abel, C.M. Giandomenico, P. Mistry, K.R. Harrap, Cancer Res. 52 (1992) 822.
[4] M. Yoshida, A.R. Khokhar, Z.H. Siddik, Cancer Res. 54 (1994) 4691.
[5] F.R. Hartley, The Chemistry of Platinum and Palladium, Wiley, New York, 1973.
[6] S. Choi, C. Filotto, M. Bisanzo, S. Delaney, D. Lagasee, J.L. Whitworth, A. Jusko, C. Li, N.A. Wood, J. Willingham, A. Schwenker, K. Spaulding, Inorg. Chem. 37 (1998) 2500.
[7] L.T. Ellis, H. Er, T.W. Hambley, Aust. J. Chem. 48 (1995) 793.
[8] M.J. Arendse, G.K. Anderson, N.P. Rath, Inorg. Chem. 38 (1999) 5864.
[9] R.A. Stockland, G.K. Anderson, N.P. Rath, Inorg. Chim. Acta 271 (1998) 236.
[10] Siemens Analytical X-ray Division, Madison, WI, 1995.
[11] N.A. Kratochwil, M. Zabel, K.J. Range, P.J. Bednarski, J. Med. Chem. 39 (1996) 2499.
[12] C.S. Jung, S.S. Lee, K.K. Kim, O.S. Jung, Y.S. Sohn, Bull. Kor. Chem. Soc. 16 (1995) 981.
[13] K.K. Kim, Y. Lee, S.S. Lee, Y.S. Sohn, Inorg. Chim. Acta 292 (1999) 52.
[14] W. Preetz, J.-G. Uttecht, Z. Naturforsch., Teil B 53 (1998) 93.
[15] S.O. Dunham, R.D. Larsen, E.H. Abbott, Inorg. Chem. 32 (1993) 2049.
[16] M.J. Arendse, G.K. Anderson, N.P. Rath, Polyhedron 32 (2001) 2495.
[17] R.N. Bose, E.L. Weaver, J. Chem. Soc., Dalton Trans. (1997) 1797.
[18] M.B. Davies, J. Austin, D.A. Partridge, Vitamin C: Its Chemistry and Biochemistry, Royal Society of Chemistry, London, 1991.
[19] W. Jabs, W. Gaube, Z. Anorg. Allgem. Chem. 514 (1984) 179.
[20] R.M. Roat, M.J. Jerardi, C.B. Kopay, D.C. Heath, J.A. Clark, J.A. DeMars, J.M. Weaver, E. Bezemer, J. Reedijk, J. Chem. Soc., Dalton Trans. (1997) 3615.