that ($1.7 \times 10^3$ $M^{-1}$) for the $Mo_2O_2$ complex. Thus, the $k_2$ for the $W_2OS$ complex should be smaller by at least 1 order of magnitude than that for the $Mo_2O_2$ complex, suggesting the stabilization of the intermediate by the sulfide bridge.

**Concluding Remarks.** The redox behaviors of all the complexes including $MoWO_2$ should be understood in a similar way, as the free energy relationship holds. Two metal ions in the $MoWO_2$ complex behave practically as a single redox center, rather than as two different redox centers. The effect of the sulfide bridge is first to make the oxidation potential more positive and retard the first oxidation process and second to stabilize the intermediate to make the reverse process ($k_{-1}$) more effective.

**Acknowledgment.** J.F.O. is grateful for an award from the Japan Society for Promotion of Science. This work was supported by a Grant-in-Aid for Scientific Research (No. 01612001) for the priority area of "Dynamic Interactions and Electronic Processes of Macromolecular Complexes" from the Ministry of Education, Science and Culture of Japan. Valuable discussions and technical assistance by Dr. Akira Nagasawa (Saitama University) are gratefully acknowledged. Helpful comments from Professor Tasuku Ito (Tohoku University) are also acknowledged.

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# Heptacoordination of Manganese(II) by the Polyazacycloalkane [21]ane$N_7$. Crystal Structure of the [Mn([21]ane$N_7$)]($ClO_4$)$_2$ Solid Compound and Thermodynamics of Complexation in Water Solution

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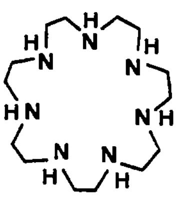
The thermodynamic parameters for the equilibrium of complexation between manganese(II) and 1,4,7,10,13,16,19-heptaazacycloheneicosane ([21]ane$N_7$) have been determined by potentiometry and microcalorimetry in 0.15 mol $dm^{-3}$ $NaClO_4$ at 25 °C. The [21]ane$N_7$ ligand forms with manganese(II), in solution, a very stable complex (log $K = 9.79$ (1)) that preserves the metal ion from air oxidation, even in alkaline solution. The thermodynamic stability of this complex in solution is mainly entropic in nature ($\Delta H^\circ = -5.0$ (5) kcal $mol^{-1}$; $T\Delta S^\circ = 8.2$ kcal $mol^{-1}$). The absence of protonated complexes in solution suggests the heptacoordination of [21]ane$N_7$ to manganese(II). This is supported by the crystal structure of the complex [Mn([21]ane$N_7$)]($ClO_4$)$_2$. Crystals of this compound are orthorhombic, space group $P22_12_1$, with $a = 9.751$ (3) Å, $b = 15.040$ (4) Å, $c = 32.781$ (5) Å, $V = 4807$ (2) Å$^3$, $Z = 8$, $d_{calc} = 1.53$ g/cm$^3$, $\mu = 7.44$ cm$^{-1}$, $F(000) = 2327.44$, and $M = 555.32$. The structure has been solved by using the heavy-atom method and $F_0$ and $\Delta F$ Fourier synthesis and was refined by least-squares methods to $R = 0.085$ ($R_w = 0.069$) for 1390 reflections having $I > 3\sigma(I)$. The asymmetric unit contains two independent [Mn([21]ane$N_7$)]$^{2+}$ complexed molecules in which manganese(II) is similarly heptacoordinated by [21]ane$N_7$, which disposes its nitrogen atoms at the vertices of an irregular polyhedron. The main difference between the two independent molecules is determined by the conformation of two chelate rings.

## Introduction

The design of metal ion receptors has been mostly realized by means of synthetic macrocyclic molecules.[2] The achievement of selective interactions between the host macrocycles and the guest metal ions has produced a rapid advancement in the field of both biomimetic and abiotic model systems.[3,4] However, many metal ions have been so far disregarded by similar studies. Complexes of manganese(II) with synthetic macrocyclic ligands are almost unknown in spite of the importance of this metal ion in human living systems as a trace element.[4]

In the course of the present study, we have observed that the polyazacycloalkane 1,4,7,10,13,16,19-heptaazacycloheneicosane, hereafter abbreviated as [21]ane$N_7$, is a particularly suitable receptor for manganese(II), being able to wrap around this metal ion and achieve heptacoordination, forming a very stable complex that preserves the metal ion from air oxidation even in alkaline solution. The crystal structure of the compound [Mn([21]ane$N_7$)]($ClO_4$)$_2$ has been solved by single-crystal X-ray analysis. The heptacoordination of manganese(II) is achieved by means of the seven nitrogen donor atoms of the ligand. As far as we are aware, this is the first time that the heptacoordination of manganese(II), achieved by only one ligand, is described in terms of the crystal structure in the solid state and the thermodynamics of complexation equilibria in aqueous solution.



[21]ane$N_7$

## Experimental Section

**Materials.** The complex [Mn([21]ane$N_7$)]($ClO_4$)$_2$ was synthesized by refluxing 20 mL of a water solution containing 0.1 mmol [21]ane$N_7$·7HCl[5] and 0.1 mmol of Mn($ClO_4$)$_2$·7$H_2O$, followed by dropwise addition of a 0.2 mol $dm^{-3}$ NaOH solution. When the pH of the reaction solution was about 9.5, solid $NaClO_4 \cdot H_2O$ (8 g) was added in small portions. On cooling, a colorless microcrystalline powder of the complex separated. Elemental analysis and magnetic susceptibility agreed with that expected for the high-spin complex. Crystals of the complex suitable for X-ray analysis were obtained by slow evaporation of the mother solution at room temperature.

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0020-1669/90/1329-1716$02.50/0

**Table I.** Crystallographic Data for $Mn([21]aneN_7)(ClO_4)_2$

| | | | |
|---|---|---|---|
| formula | $C_{14}H_{35}N_7Cl_2MnO_8$ | $d_{calc}$, $g/cm^3$ | 1.53 |
| mol wt | 555.32 | $\mu$, $cm^{-1}$ | 7.44 |
| space group | $P22_12_1$ | radiation | graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.7107 Å) |
| $a$, Å | 9.751 (3) | | |
| $b$, Å | 15.040 (4) | | |
| $c$, Å | 32.781 (5) | temp. °C | 25 |
| $V$, $Å^3$ | 4807 (2) | $R^a$ | 0.085 |
| $Z$ | 8 | $R_w{}^b$ | 0.069 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

**Emf Measurements.** All potentiometric measurements were carried out in 0.15 mol $dm^{-3}$ $NaClO_4$ (C. Erba ACS grade), purified according to a previously reported procedure.[6] The stock solution of manganese(II) chloride was prepared in doubly distilled water and the concentration of the metal ion determined by standard methods. $CO_2$-free NaOH and HCl solutions, used in the titrations, were prepared and stored in an argon atmosphere and standardized as described in ref 7. The hydrochloride salt of $[21]aneN_7$, employed as a starting material, was obtained as described in ref 5, and the protonation constants of $[21]aneN_7$ are from ref 8. The potentiometric titrations were carried out by using equipment that has been fully described.[9] All solutions used were exhaustively deaerated by an argon flow and kept under the same atmosphere during the measurements. Three titrations were used for the investigated system. The computer program SUPERQUAD[10] was used to process emf data and to calculate the stability constants by following the procedure reported in ref 11, footnote 18.

**Microcalorimetry.** The enthalpy change for the reaction between manganese(II) and $[21]aneN_7$ was obtained, by means of a Thermal Activity Monitor Model 2277 (Termometric AB) microcalorimeter, by acid dissociation of the complex $[Mn([21]aneN_7)]^{2+}$ in a 0.15 mol $dm^{-3}$ $NaClO_4$ water solution. Corrections for the heat of protonation of $[21]aneN_7$ and for the heats of dilution of the reactant solutions were taken into account.

**Collection and Reduction of X-ray Intensity Data.** A crystal of $[Mn([21]aneN_7)](ClO_4)_2$ was mounted on a Enraf-Nonius CAD4 automatic diffractometer. A summary of crystallographic data is reported in Table I. Cell constants were determined by a least-squares fitting of 25 accurately centered reflections. During data collection the intensities of three standard reflections were monitored periodically for stability control. A total of 4760 reflections were collected in the range $5° < 2\theta < 50°$.

**Solution and Refinement of the Structure.** A total of 1390 reflections having $I > 3\sigma(I)$ were used in the structure analysis. An absorption correction[12] was applied, and the structure was solved by using the heavy-atom method, which showed the presence of two independent $[Mn([21]aneN_7)]^{2+}$ cations. Subsequent $F_o$ and $\Delta F$ Fourier syntheses showed the positions of all non-hydrogen atoms; the hydrogen atoms were introduced in calculated positions. Two perchlorate anions, lying on a 2-fold axis, have 0.5 multiplicity, and therefore five independent perchlorate anions are present. The oxygen atoms of three independent perchlorates are disordered, and, therefore, two different models were assigned to these anions. Rather high thermal parameters were found for the atoms of the ethylenic chains of the macrocyclic ligands as a consequence of some degree of disorder that is also present in these chains. Manganese and chlorine atoms were refined anisotropically, whereas the lighter atoms were refined isotropically. Table II shows the final atomic coordinates for non-hydrogen atoms with estimated standard deviations; Table III reports some interesting bond distances and angles.

All of the calculations were performed with the SHELX-76[13] program package. The molecular plots were produced by the program ORTEP.[14]

**Table II.** Positional Parameters ($\times 10^4$) and $U_{eq}$ or $U_{iso}$ ($Å^2 \times 10^3$) for $[Mn([21]aneN_7)](ClO_4)_2$

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| Mn1 | −619 (5) | −2527 (5) | −1631 (1) | 39 (4) |
| Mn2 | −4562 (5) | −2464 (4) | −4131 (2) | 38 (4) |
| Cl1 | −4130 (13) | −2676 (11) | −5792 (4) | 80 (11) |
| Cl2 | −491 (16) | −1045 (9) | −3156 (4) | 73 (10) |
| Cl3 | −5372 (17) | −4871 (8) | −2850 (4) | 81 (10) |
| Cl4$^a$ | −303 (25) | −5000 | −5000 | 133 (22) |
| Cl5$^a$ | −2457 (21) | −5000 | 0 | 69 (13) |
| N1 | −397 (70) | −4003 (38) | −1179 (16) | 205 (23) |
| N2 | −280 (54) | −1913 (32) | −874 (14) | 154 (19) |
| N3 | −1198 (52) | −815 (33) | −1590 (16) | 150 (22) |
| N4 | 1663 (46) | −1807 (29) | −1679 (16) | 145 (18) |
| N5 | 980 (45) | −3524 (31) | −2126 (15) | 153 (19) |
| N6 | −1690 (42) | −2754 (30) | −2290 (12) | 133 (16) |
| N7 | −2978 (43) | −3089 (28) | −1458 (14) | 117 (17) |
| C1 | 12 (55) | −3435 (33) | −784 (16) | 113 (20) |
| C2 | −312 (57) | −2695 (35) | −661 (14) | 124 (20) |
| C3 | −1658 (53) | −1502 (34) | −902 (16) | 125 (19) |
| C4 | −1543 (59) | −721 (33) | −1181 (15) | 118 (21) |
| C5 | −90 (58) | −547 (37) | −1856 (16) | 160 (26) |
| C6 | 1352 (63) | −853 (40) | −1727 (21) | 172 (28) |
| C7 | 2337 (70) | −2046 (41) | −2054 (20) | 156 (31) |
| C8 | 2456 (56) | −3015 (33) | −2067 (17) | 128 (21) |
| C9 | 409 (57) | −3219 (32) | −2503 (16) | 164 (23) |
| C10 | −1168 (38) | −3525 (29) | −2510 (13) | 89 (15) |
| C11 | −3185 (53) | −2894 (33) | −2144 (16) | 126 (20) |
| C12 | −3421 (71) | −3470 (44) | −1779 (22) | 200 (34) |
| C13 | −2716 (61) | −3837 (41) | −1165 (17) | 150 (23) |
| C14 | −1479 (67) | −4389 (40) | −1187 (21) | 294 (31) |
| N8 | −6901 (38) | −2236 (27) | −4400 (13) | 98 (15) |
| N9 | −5080 (48) | −3630 (26) | −4632 (11) | 103 (16) |
| N10 | −3504 (39) | −3890 (25) | −3865 (11) | 79 (12) |
| N11 | −2157 (35) | −2717 (27) | −4350 (11) | 82 (12) |
| N12 | −3886 (51) | −1029 (29) | −4523 (13) | 141 (18) |
| N13 | −3927 (39) | −1435 (26) | −3632 (12) | 91 (13) |
| N14 | −6040 (35) | −2629 (32) | −3524 (11) | 104 (14) |
| C15 | −7142 (42) | −2747 (29) | −4755 (12) | 82 (16) |
| C16 | −6586 (57) | −3625 (37) | −4722 (18) | 137 (22) |
| C17 | −4816 (55) | −4313 (28) | −4414 (14) | 114 (19) |
| C18 | −4263 (49) | −4526 (28) | −4041 (13) | 95 (17) |
| C19 | −2162 (61) | −3909 (40) | −3930 (18) | 150 (25) |
| C20 | −1583 (50) | −3125 (32) | −4099 (17) | 105 (19) |
| C21 | −1845 (68) | −1895 (42) | −4528 (20) | 142 (29) |
| C22 | −2633 (58) | −1396 (39) | −4760 (16) | 139 (24) |
| C23 | −3844 (60) | −464 (34) | −4207 (18) | 133 (24) |
| C24 | −4206 (82) | −759 (44) | −3765 (21) | 202 (35) |
| C25 | −4678 (84) | −1647 (49) | −3304 (25) | 279 (43) |
| C26 | −6006 (69) | −2137 (43) | −3251 (21) | 182 (34) |
| C27 | −7528 (53) | −2716 (40) | −3685 (15) | 119 (21) |
| C28 | −7794 (69) | −2099 (39) | −4053 (19) | 169 (30) |
| O11$^a$ | −3629 (71) | −1975 (41) | −5979 (20) | 82 (23) |
| O12$^a$ | −4812 (55) | −3010 (34) | −6100 (17) | 69 (18) |
| O13$^a$ | −4603 (10) | −2099 (62) | −5567 (29) | 109 (41) |
| O14$^a$ | −2945 (84) | −3031 (47) | −5807 (25) | 102 (30) |
| O15$^a$ | −3724 (37) | −3022 (70) | −5444 (34) | 268 (51) |
| O16$^a$ | −5084 (55) | −3053 (59) | −5626 (29) | 147 (40) |
| O21$^a$ | −1261 (57) | −304 (35) | −3390 (19) | 63 (20) |
| O22$^a$ | −1378 (81) | −1609 (57) | −2968 (26) | 131 (31) |
| O23$^a$ | −417 (36) | −1309 (96) | −3535 (47) | 253 (65) |
| O24$^a$ | 910 (94) | −1169 (56) | −3012 (26) | 169 (36) |
| O25$^a$ | −717 (58) | −1931 (36) | −3234 (18) | 69 (19) |
| O26$^a$ | −583 (16) | −685 (71) | −3531 (35) | 144 (37) |
| O27$^a$ | 865 (85) | −676 (50) | −3115 (23) | 95 (28) |
| O28$^a$ | −1138 (54) | −779 (35) | −2807 (17) | 61 (18) |
| O31 | −4247 (47) | −4483 (25) | −3059 (13) | 172 (17) |
| O32 | −5451 (56) | −5695 (30) | −3040 (14) | 199 (21) |
| O33 | −5515 (51) | −4888 (31) | −2460 (15) | 191 (21) |
| O34 | −6414 (71) | −4478 (41) | −3010 (22) | 286 (40) |
| O41 | 770 (51) | −4575 (29) | −4753 (14) | 195 (22) |
| O42 | −1018 (57) | −5616 (32) | −4798 (16) | 225 (28) |
| O51$^a$ | −2936 (80) | −4274 (49) | −194 (21) | 139 (29) |
| O52$^a$ | −1898 (26) | −5485 (77) | −357 (36) | 263 (53) |
| O53$^a$ | −3287 (69) | −5187 (44) | −371 (21) | 94 (21) |
| O54$^a$ | −1432 (70) | −4327 (47) | 20 (26) | 130 (26) |

[a] Atoms with population parameters of 0.5.

## Results and Discussion

**Description of the Structure.** The structure of $[Mn([21]aneN_7)](ClO_4)_2$ consists of $[Mn([21]aneN_7)]^{2+}$ cations and disordered perchlorate anions. The asymmetric unit contains two independent complexed molecules (Figures 1 and 2) in which the

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**Table III.** Selected Distances (Å) and Angles (deg) for $[Mn([21]aneN_7)](ClO_4)_2$

| | | | |
|---|---|---|---|
| Distances | | | |
| Mn1-N1 | 2.68 (6) | Mn2-N8 | 2.47 (4) |
| Mn1-N2 | 2.67 (5) | Mn2-N9 | 2.46 (4) |
| Mn1-N3 | 2.64 (5) | Mn2-N10 | 2.53 (4) |
| Mn1-N4 | 2.48 (4) | Mn2-N11 | 2.48 (3) |
| Mn1-N5 | 2.70 (5) | Mn2-N12 | 2.60 (4) |
| Mn1-N6 | 2.43 (4) | Mn2-N13 | 2.34 (4) |
| Mn1-N7 | 2.51 (4) | Mn2-N14 | 2.47 (4) |
| Angles | | | |
| N6-Mn1-N7 | 76 (1) | N13-Mn2-N14 | 70 (1) |
| N5-Mn1-N7 | 118 (1) | N12-Mn2-N14 | 129 (1) |
| N5-Mn1-N6 | 69 (1) | N12-Mn2-N13 | 74 (1) |
| N4-Mn1-N7 | 169 (2) | N11-Mn2-N14 | 140 (1) |
| N4-Mn1-N6 | 113 (2) | N11-Mn2-N13 | 93 (1) |
| N4-Mn1-N5 | 72 (1) | N11-Mn2-N12 | 75 (1) |
| N3-Mn1-N7 | 97 (1) | N10-Mn2-N14 | 83 (1) |
| N3-Mn1-N6 | 95 (2) | N10-Mn2-N13 | 102 (1) |
| N3-Mn1-N5 | 134 (2) | N10-Mn2-N12 | 140 (1) |
| N3-Mn1-N4 | 77 (2) | N10-Mn2-N11 | 65 (1) |
| N2-Mn1-N7 | 91 (2) | N9-Mn2-N14 | 110 (1) |
| N2-Mn1-N6 | 159 (1) | N9-Mn2-N13 | 175 (1) |
| N2-Mn1-N5 | 133 (1) | N9-Mn2-N12 | 108 (1) |
| N2-Mn1-N4 | 78 (2) | N9-Mn2-N11 | 84 (1) |
| N2-Mn1-N3 | 69 (2) | N9-Mn2-N10 | 73 (1) |
| N1-Mn1-N7 | 71 (2) | N8-Mn2-N14 | 76 (1) |
| N1-Mn1-N6 | 114 (2) | N8-Mn2-N13 | 114 (1) |
| N1-Mn1-N5 | 80 (2) | N8-Mn2-N12 | 87 (1) |
| N1-Mn1-N4 | 109 (2) | N8-Mn2-N11 | 142 (1) |
| N1-Mn1-N3 | 143 (2) | N8-Mn2-N10 | 128 (1) |
| N1-Mn1-N2 | 76 (2) | N8-Mn2-N9 | 71 (1) |

manganese ion shows similar coordination. In both cases the metal ion is surrounded by seven nitrogen atoms of the macrocyclic ligand, which forms five-membered chelate rings in the gauche conformation. The main difference between the two complexed molecules is determined by the conformation of the two chelate rings, which terminate in N6 (molecule 1) and in N14 (molecule 2), respectively. The other parts of the two molecules present opposite chirality. The Mn–N bond distances (Table III) in both conformational isomers range from 2.43 (4) to 2.70 (5) Å (molecule 1) and from 2.34 (4) to 2.60 (4) Å (molecule 2). Most of these distances are significantly longer than those observed in other 7-coordinated manganese(II) compounds.[15] The bond angles around Mn1 and Mn2 (Table III), as well as the bond angles inside the macrocyclic framework, show that the ligand $[21]aneN_7$ disposes its seven nitrogen donor atoms at the vertices of an irregular polyhedron, achieving heptacoordination at the expense of some intramolecular strain. This is also reflected in some C–C and C–N bond distances that are slightly different from the classical values. Crystals of $[Mn([21]aneN_7)](ClO_4)_2$ are isomorphic with those of the previous reported $[Ni([21]aneN_7)](ClO_4)_2$ complex.[16] In the nickel(II) compound, $[21]aneN_7$ acts as hexadentate ligand, forming a distorted octahedral complex in which a eight-membered chelate ring contains the uncoordinated nitrogen. No strain was observed in the ligand $[21]aneN_7$ coordinated to the nickel(II) ion.

**Solution Study.** The equilibrium constant related to the formation reaction of $[Mn([21]aneN_7)]^{2+}$ complex ($\log K = 9.79$ (1)), determined by potentiometric titration in a 0.15 mol dm$^{-3}$ $NaClO_4$ water solution at 25 °C, is the lowest among those determined under the same conditions for the analogous complexes of iron(II),[17] cobalt(II),[18] nickel(II),[16] copper(II),[17] zinc(II),[8] and cadmium(II).[19] However, the complex is very stable, and upon complexation, the $[21]aneN_7$ ligand preserves the manganese(II) from air oxidation in alkaline solution; only at very high $OH^-$ concentration can the formation of manganese(II) hydroxide occur and subsequent oxidation take place. Among the above-mentioned metal ions, only manganese(II) does not form protonated complexed species with $[21]aneN_7$ in solution, indicating that no uncoordinated nitrogen atoms available for protonation are present in $[Mn([21]aneN_7)]^{2+}$; in other words, the heptacoordination of manganese(II), observed in the solid state, is likely preserved in solution. The thermodynamic parameters, determined for the formation of $[Mn([21]aneN_7)]^{2+}$ ($\Delta H° = -5.0$ (5) kcal mol$^{-1}$; $T\Delta S^0 = 8.2$ kcal mol$^{-1}$), show that the stability of this complex is mainly entropic in nature. This can be attributed to the large desolvation effects of the heptadentate macrocyclic ligand occurring upon full coordination to manganese(II). On the other hand, on the basis of the long Mn–N bond distances observed in the solid complex, a small enthalpic contribution to the stability of $[Mn([21]aneN_7)]^{2+}$ complex in solution is expected.

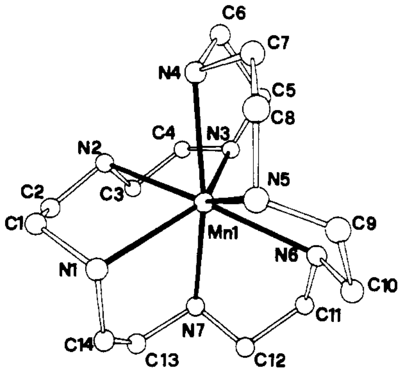

**Figure 1.** ORTEP view of molecule 1 in $[Mn([21]aneN_7)](ClO_4)_2$. For the sake of clarity, a thermal parameter $U$ of 0.04 Å$^2$ was assigned to all atoms.

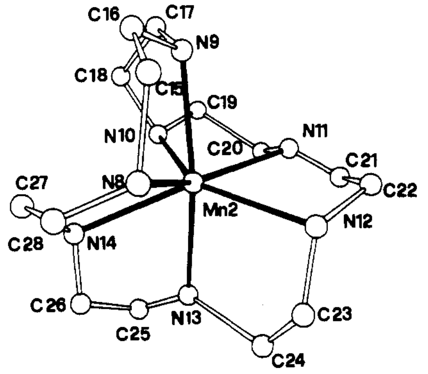

**Figure 2.** ORTEP view of molecule 2 in $[Mn([21]aneN_7)](ClO_4)_2$. For the sake of clarity, a thermal parameter $U$ of 0.04 Å$^2$ was assigned to all atoms.

**Acknowledgment.** Financial support from the Italian "Ministero della Pubblica Istruzione" is gratefully acknowledged.

**Registry No.** $[Mn([21]aneN_7)](ClO_4)_2$, 126218-27-7.

**Supplementary Material Available:** Listings of positional parameters for non-hydrogen atoms (Table S1), anisotropic thermal parameters (Table S2), positional parameters for the hydrogen atoms (Table S3), and complete bond distances and angles (Table S5) (9 pages); a listing of observed and calculated structure factors (Table S4) (7 pages). Ordering information is given on any current masthead page.

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