

Structural and Magnetic Characterization of Manganese(III) Complexes of 1,4,8,11-Tetraazacyclotetradecane (Cyclam)

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The syntheses and structural and magnetic properties of a series of complexes of the type $[\text{Mn}(\text{cyclam})\text{X}_2]\text{Y}$ (where cyclam is 1,4,8,11-tetraazacyclotetradecane, $\text{C}_{10}\text{H}_{24}\text{N}_4$, and X and Y are monoanionic species) are described. The new complex $[\text{Mn}(\text{cyclam})(\text{NO}_3)_2]\text{NO}_3$, (**1**), $\text{MnC}_{10}\text{H}_{24}\text{N}_7\text{O}_9$, crystallizes in the monoclinic space group $\text{C}2/c$ with four molecules in a cell of dimensions $a = 12.977(2)$, $b = 8.904(2)$, $c = 15.562(2)$ Å, $\beta = 106.76(1)^\circ$. The structure has been refined to a final R -factor of 0.0369 based on 930 observed data. The dichloro complex $[\text{Mn}(\text{cyclam})\text{Cl}_2]\text{NO}_3$, (**2**), $\text{MnC}_{10}\text{H}_{24}\text{N}_5\text{O}_3\text{Cl}_2$, crystallizes in the monoclinic space group $\text{P}2_1/n$ with two molecules in a cell of dimensions $a = 6.547(2)$, $b = 13.698(4)$, $c = 9.376(2)$ Å, $\beta = 101.70(2)^\circ$. The structure has been refined to $R = 0.0255$ based on 1909 observed data. The dibromo species $[\text{Mn}(\text{cyclam})\text{Br}_2]\text{Br}$, (**3**), $\text{MnC}_{10}\text{H}_{24}\text{N}_4\text{Br}_3$, crystallizes in the tetragonal space group $\text{P}4_2/m$ with two molecules in a cell of dimensions $a = 7.971(2)$, $c = 13.002(4)$ Å. The structure has been refined to $R = 0.0589$ based on 664 observed intensities. The thiocyanato complex $[\text{Mn}(\text{cyclam})(\text{NCS})_2]\text{NCS}$, (**4**), $\text{MnC}_{13}\text{H}_{24}\text{N}_7\text{S}_3$, crystallizes in the monoclinic space group $\text{P}2_1/c$ with four molecules in a cell of dimensions $a = 10.767(2)$, $b = 12.940(2)$, $c = 14.441(3)$ Å, $\beta = 99.004(16)^\circ$. The structure has been refined to $R = 0.0349$ based on 1764 observed intensities. All four of these structures adopt the expected *trans* geometry, and all exhibit the axial elongation expected for d^4 complexes. In addition, another new *trans* complex, of formulation *trans*- $[\text{Mn}(\text{cyclam})(\text{CN})_2]\text{ClO}_4$, has been synthesized, as has the new *cis* complex *cis*- $[\text{Mn}(\text{cyclam})\text{Br}_2]\text{Br}$. The magnetic properties of the complexes are all consistent with their formulation as monomeric high-spin d^4 systems, all exhibiting room-temperature moments in the vicinity of the spin-only value of $4.9 \mu_B$. In the case of **2** there is a significant magnetic interaction between adjacent manganese centers, which can be explained in the light of the structure.

In recent years there has been considerable research interest in the synthesis and characterization of manganese(III) complexes of synthetic macrocyclic ligands with nitrogen donors. This interest is stimulated, to a large extent, by the observation that a high-valent manganese porphyrin complex may be involved in the photosynthetic process.¹ More recently, several manganese(III) complexes of porphyrins and Schiff bases have been shown to serve as catalysts for the epoxidation of alkenes and for related reactions.^{2–5}

Manganese(III) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) have been reported by Poon⁶ and by Bryan,⁷ who also examined the room-temperature magnetic properties of the complexes in order to demonstrate that they should be formulated as high-spin d^4 manganese(III) systems. No definitive structural study has appeared, but the cyclam complexes of manganese of the general type $[\text{Mn}(\text{cyclam})\text{X}_2]\text{Y}$ (where X and Y are anionic species) have been formulated as *trans*-octahedral systems.

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We here report the synthesis and solid-state structural characterization of four complexes of this general type, along with the variable-temperature magnetic properties of these species.

Experimental

Magnetic susceptibility measurements were performed by the Faraday method in the temperature range 4–300 K using instrumentation described elsewhere.^{8,9} The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

Synthesis of the complexes

1. *trans*-Dinitrato(1,4,8,11-tetraazacyclotetradecane)manganese(III) nitrate, *trans*- $[\text{Mn}(\text{cyclam})(\text{NO}_3)_2]\text{NO}_3$. Cyclam (0.600 g, 3.00 mmol) was dissolved in ethanol (15 ml, 96%). Manganese(II) nitrate hexahydrate (0.834 g, 3.00 mmol) was added, and the solution was left with stirring for 1 h. The solution quickly turned green, and an olive-green

precipitate separated. This solid (a) was filtered and washed with acetone. It was considered to be a mixture of monomeric and dimeric manganese complexes with cyclam, consisting mainly of the dimeric nitrate mentioned below and of the title complex. The yield was 0.357 g. The dark-green filtrate was evaporated in air to give 0.367 g of dark-green crystals (b), which were found analytically to consist mainly of [Mn(cyclam)O]₂(NO₃)₃·3H₂O. The solid (b) (0.200 g, ca. 0.25 mmol) was extracted on a filter with water (4 ml). Nitric acid (4 ml, 4 M) was added, and the solution was left overnight. By the next day large, shining, dark-blue crystals had separated. They were filtered off and washed with ethanol (96 %). Yield: 0.106 g [ca. 48 % based on manganese in solid (b)]. Anal. [Mn(C₁₀H₂₄N₄)(NO₃)₂](NO₃): Mn, C, N, H. The same compound in a yield of 0.112 g was obtained from crude product (a) (0.200 g) by the same procedure.

2. *trans-Dichloro(1,4,8,11-tetraazacyclotetradecane)manganese(III) nitrate*, trans-[Mn(cyclam)Cl₂]NO₃. trans-[Mn(cyclam)(NO₃)₂]NO₃ (0.200 g, 0.453 mmol) was extracted on a filter with water (4 ml). A mixture of nitric acid (2 ml, 4 M) and hydrochloric acid (0.4 ml, 4 M) was added, and the solution was left overnight. By the next day, large green crystals had separated. They were filtered and washed with ethanol (96 %). Yield: 0.072 g (41 %). Anal. [Mn(C₁₀H₂₄N₄)Cl₂](NO₃): Mn, C, N, H, Cl.

3. *trans-Dibromo(1,4,8,11-tetraazacyclotetradecane)manganese(III) bromide*, trans-[Mn(cyclam)Br₂]Br. A crude product (a), 1.109 g, was obtained exactly as described in preparation 1, but from manganese(II) bromide tetrahydrate (0.867 g, 3.00 mmol). As before, the solid was considered as consisting of a mixture of monomeric and dimeric complexes of manganese with cyclam. The corresponding green crystals (b) were obtained in a yield of 106 mg. They were found analytically to consist of practically pure [Mn(cyclam)O]₂Br₃·5H₂O. The solid (b) (0.100 g, 0.115 mmol) was extracted on a filter with water (5 ml), and hydrobromic acid (5 ml, 1 M) was added. Soon afterwards, oblong, dark-green crystals separated. These crystals, considered to be dimeric, were transformed to emerald-green crystals of the monomeric dibromo complex when left in the solution overnight. The resulting compound was filtered and washed with ethanol (96 %). Yield: 0.031 g (25 %). Anal. [Mn(cyclam)Br₂]Br: Mn, C, N, H, Br. The same compound in a yield of 0.065 was obtained from crude product (a) (0.100 g).

4. *trans-Dichloro(1,4,8,11-tetraazacyclotetradecane)manganese(III) chloride pentahydrate*, trans-[Mn(cyclam)Cl₂]Cl·5H₂O. A crude product (a), 0.775 g was prepared exactly as described in preparation 1, but from manganese(II) chloride tetrahydrate (0.0591 g, 3.00 mmol). The solid consisted of a mixture of monomeric and dimeric complexes of manganese with cyclam. The corresponding dark-green crystals (b) in a yield of 0.211 g were obtained.

They were found analytically to consist mainly of [Mn(cyclam)O]₂Cl₃·3H₂O. The solid (b) (0.200 g, 0.285 mmol) was extracted on a filter with water (5 ml), and hydrochloric acid (5 ml, 4 M) was added. The solution changed color from dark green to apple green, and soon needle-shaped crystals separated. They were filtered and washed with ethanol (96 %). Yield: 0.082 g (32 %). Anal. [Mn(cyclam)Cl₂]Cl·5H₂O: Mn, C, N, H, Cl. The same compound in a yield of 0.121 g was obtained from crude product (a) (0.200 g).

5. *trans-Dithiocyanato(1,4,8,11-tetraazacyclotetradecane)manganese(III) thiocyanate*, trans-[Mn(cyclam)(NCS)₂](NCS). trans-[Mn(cyclam)Cl₂]Cl·5H₂O (0.065 g, 0.144 mmol) was dissolved in water. A concentrated solution of potassium thiocyanate (0.2 g, 2.0 mmol) was added. Soon afterwards, large yellow-brown crystals separated. They were washed with ethanol (96 %). Yield: 0.041 g (65 %). Anal. [Mn(C₁₀H₂₄N₄)(NCS)₂](NCS): Mn, C, H, S.

6. *trans-Dicyano(1,4,8,11-tetraazacyclotetradecane)manganese(III) perchlorate*, trans-[Mn(cyclam)(CN)₂]ClO₄. trans-[Mn(cyclam)Cl₂]Cl·5H₂O (0.150 g, 0.332 mmol) was dissolved in water (1.5 ml). Sodium cyanide (0.060 g, 0.82 mmol) was added with stirring. When the solution had turned red, a solution of sodium perchlorate (1 M) was added slowly. The yellow crystals that separated were filtered and washed with a solution of sodium perchlorate (1 M) and with ethanol (96 %). Yield: 0.058 g (43 %). Anal. [Mn(cyclam)(CN)₂]ClO₄: Mn, C, H, N, Cl.

7. *cis-Dibromo(1,4,8,11-tetraazacyclotetradecane)manganese(III) bromide monohydrate*, cis-[Mn(cyclam)Br₂]Br·H₂O. [Mn(cyclam)O]₂Br₃·5H₂O (0.095 g, 0.109 mmol) was treated on a filter with a small amount of hydrobromic acid (9.5 ml, 9 M). The green crystals immediately changed color to dark red. The solvent was removed by filtration after a few minutes, and the solid was washed with ethanol (96 %). Yield: 0.091 g (81 %). Anal. [Mn(C₁₀H₂₄N₄)Br₂]·H₂O: Mn, C, N, H, Br.

X-Ray structure determinations. The structures of four complexes were determined. The complexes are [Mn(cyclam)(NO₃)₂]NO₃ (1), [Mn(cyclam)Cl₂]NO₃ (2), [Mn(cyclam)Br₂]Br (3) and [Mn(cyclam)(NCS)₂]NCS (4). All four structures were determined at room temperature (294 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($K\alpha_1 = 0.70926 \text{ \AA}$; $K\alpha_2 = 0.71354 \text{ \AA}$) and a graphite monochromator. Cell constants were determined by least-squares refinement of the angular settings of 25 high-intensity data points in the range $20 \leq 2\theta \leq 25^\circ$. Empirical absorption corrections were applied to the data. The intensities of three standard reflections, monitored after every 100 data points, showed only the fluctuations expected from counting statistics. Crystal data and experimental parameters are listed in Table 1. The structures were solved by direct methods, and refined by full-matrix

Table 1. Crystallographic and data collection parameters.

| Complex | 1 | 2 | 3 | 4 |
|---|---|--|--|---|
| Formula | MnC ₁₀ H ₂₄ N ₇ O ₉ | MnC ₁₀ H ₂₄ N ₅ O ₃ Cl ₂ | MnC ₁₀ H ₂₄ N ₄ Br ₃ | MnC ₁₃ H ₂₄ N ₇ S ₃ |
| Color and habit | Blue, needle | Green, lath | Green, prism | Orange, prism |
| Dimensions/mm | 0.10×0.18×0.18 | 0.60×0.30×0.24 | 0.90×0.47×0.50 | 0.26×0.40×0.40 |
| System | Monoclinic | Monoclinic | Tetragonal | Monoclinic |
| Space group | <i>C2/c</i> | <i>P2₁/n</i> | <i>P4₂/m</i> | <i>P2₁/c</i> |
| Cell dimensions | <i>a</i> = 12.977(2) Å <i>b</i> = 8.904(2) Å <i>c</i> = 15.562(2) Å β = 106.76(1)° | <i>a</i> = 6.547(2) Å <i>b</i> = 13.698(4) Å <i>c</i> = 9.376(2) Å β = 101.70(2)° | <i>a</i> = 7.971(2) Å <i>c</i> = 13.002(4) Å | <i>a</i> = 10.767(2) Å <i>b</i> = 12.940(4) Å <i>c</i> = 14.441(3) Å β = 99.004(16)° |
| Volume/Å ³ | 1721.7(4) | 823.4(4) | 826.2(3) | 1987.2(6) |
| Z | 4 | 2 | 2 | 4 |
| <i>D</i> (calc.)/g cm ⁻³ | 1.498 | 1.566 | 1.990 | 1.436 |
| <i>F</i> (000) | 960 | 404 | 484 | 896 |
| Absorption coefficient/mm ⁻¹ | 0.80 | 1.11 | 7.95 | 0.95 |
| Index ranges | 0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 11 -19 ≤ <i>l</i> ≤ 19 | 0 ≤ <i>h</i> ≤ 9 0 ≤ <i>k</i> ≤ 19 -13 ≤ <i>l</i> ≤ 13 | 0 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 18 | -6 ≤ <i>h</i> ≤ 12 -6 ≤ <i>k</i> ≤ 15 -17 ≤ <i>l</i> ≤ 17 |
| Scan range/° | 4 ≤ 2 θ ≤ 50 | 4 ≤ 2 θ ≤ 60 | 4 ≤ 2 θ ≤ 60 | 4 ≤ 2 θ ≤ 50 |
| No. of reflections | 1713 | 2718 | 1429 | 4014 |
| Unique reflections, <i>R</i> _{int} | 1507, 0.0183 | 2424, 0.0149 | 1262, 0.0351 | 3514, 0.0121 |
| Observed reflections | 930 [<i>I</i> > 3 σ (<i>I</i>)] | 1909 [<i>I</i> > 3 σ (<i>I</i>)] | 664 [<i>I</i> > 3 σ (<i>I</i>)] | 1764 [<i>I</i> > 3 σ (<i>I</i>)] |
| <i>R</i> ^a | 0.0369 | 0.0255 | 0.0589 | 0.0349 |
| <i>wR</i> ^b | 0.0470 | 0.0283 | 0.0773 | 0.0393 |
| <i>S</i> (goodness of fit) | 0.88 | 1.34 | 0.67 | 1.08 |
| Maximum and minimum peaks in difference Fourier/eÅ ⁻³ | 0.34, -0.42 | 0.21, -0.32 | 1.11, -1.59 | 0.29, -0.25 |

$$^a R = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|, \quad ^b wR = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}.$$

least-squares techniques; all programs (including atomic scattering factors and dispersion corrections) were from the SHELXTL-PLUS system.¹⁰

[Mn(cyclam)(NO₃)₂]/NO₃, (1). The complex crystallizes as blue prisms in the space group *C2/c* of the monoclinic system, with four molecules in the unit cell. Hydrogen

atoms were refined isotropically while other atoms were refined anisotropically. The final values of the agreement factors were *R* = 0.0369, *wR* = 0.0470, based on 930 independent intensities with *I* > 3 σ (*I*). In the final cycle of least-squares, no parameter exhibited a shift of more than 0.15 σ , indicating that the refinement had converged. A final difference Fourier was featureless. Positional parameters are listed in Table 2.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Mn(cyclam)(NO₃)₂]/NO₃ (1).

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) ^a |
|-------|----------|----------|----------|----------------------------|
| Mn | 0 | 0 | 5000 | 19(1) |
| N(1) | 486(3) | -1817(5) | 5816(3) | 24(1) |
| C(2) | 1068(5) | -1238(6) | 6721(3) | 33(2) |
| C(3) | 1741(4) | 75(8) | 6610(3) | 33(2) |
| N(4) | 1024(4) | 1171(5) | 6011(3) | 24(1) |
| C(5) | 1635(4) | 2407(6) | 5742(4) | 33(2) |
| C(6) | 921(5) | 3534(6) | 5117(4) | 35(2) |
| C(7) | 368(4) | 2952(6) | 4185(4) | 25(2) |
| N(10) | -1739(3) | 1413(5) | 5837(2) | 27(1) |
| O(1) | -1332(2) | 213(4) | 5623(2) | 31(1) |
| O(2) | -2449(3) | 1281(4) | 6217(2) | 33(1) |
| O(3) | -1420(3) | 2647(4) | 5662(2) | 32(1) |
| N(20) | 0 | 3308(7) | 7500 | 34(2) |
| O(4) | 0 | 1889(6) | 7500 | 36(2) |
| O(5) | 630(4) | 3983(5) | 7176(3) | 56(2) |

^aEquivalent isotropic *U*, defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

[Mn(cyclam)Cl₂]/NO₃, (2). The complex crystallizes as green laths in the space group *P2₁/n* of the monoclinic system with two formula units in the unit cell. Hydrogen atoms were refined as for 1. Final values of agreement factors were *R* = 0.0255, *wR* = 0.0283, based on 1909 independent intensities with *I* > 3.0 σ (*I*). In the final cycle of least-squares, no parameter exhibited a shift of more than 0.10 σ , indicating that the refinement had converged. A final difference Fourier was featureless. Atomic parameters are listed in Table 3.

[Mn(cyclam)Br₂]/Br, (3). The complex crystallizes as green prisms in the space group *P4₂/m* of the tetragonal system, with two formula units in the unit cell. Hydrogen atoms were placed in calculated positions (C-H = 0.96 Å), while other atoms were refined anisotropically. The final values of the conventional agreement factors were *R* = 0.0589, *wR* = 0.0773, based on 664 independent intensities with *I* > 3 σ (*I*). In the final cycle of least-squares, no parameter exhibited a shift of more than 0.02 σ , indicating that the refinement had converged. A final difference Fourier was

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for [Mn(cyclam)Cl₂]NO₃ (2).

| Atom | x | y | z | U(eq) ^a |
|-------|------------|----------|------------|--------------------|
| Mn | -5000 | 5000 | 5000 | 23(1) |
| N(1) | -3260(2) | 5896(1) | 3988(1) | 29(1) |
| C(2) | -3782(3) | 5660(1) | 2410(2) | 40(1) |
| C(3) | -4001(3) | 4568(2) | 2255(2) | 41(1) |
| N(4) | -5580(2) | 4243(1) | 3095(1) | 31(1) |
| C(5) | -5710(3) | 3164(1) | 3191(2) | 44(1) |
| C(6) | -7273(3) | 2834(1) | 4085(2) | 48(1) |
| C(7) | -6669(3) | 3044(1) | 5698(2) | 40(1) |
| Cl(1) | -8279(1) | 5975(1) | 4085(1) | 36(1) |
| N | 0 | 5000 | 0 | 59(1) |
| O(1) | -1818(12) | 5015(10) | -461(8) | 106(4) |
| O(2) | 421(18) | 4183(4) | 982(10) | 70(2) |
| O(3) | 1515(18) | 5425(9) | 139(13) | 75(4) |
| O(11) | 1020(43) | 4215(21) | 475(41) | 64(7) |
| O(12) | 684(59) | 5680(15) | -399(35) | 49(6) |
| O(13) | -1631(141) | 4664(69) | -1018(160) | 89(31) |

^aSee Table 2.

featureless. The atomic positional parameters, along with their estimated standard deviations, are presented in Table 4.

[Mn(cyclam)(NCS)₂]NCS, (4). The complex crystallizes as orange prisms in the space group $P2_1/c$ of the monoclinic system, with four formula units per cell. Hydrogen atoms were treated as for (3). The agreement factors were $R = 0.0349$, $wR = 0.0393$, based on 1764 independent data with $I > 3\sigma(I)$. In the final cycle of least-squares, no parameter exhibited a shift of more than 0.09σ , indicating that the refinement had converged. A final difference Fourier was featureless. Positional parameters are given in Table 5. Hydrogen atoms and anisotropic thermal parameters for all four structures are available as supplementary material from one of the authors (D.J.H.).

Results and discussion

Synthetic aspects. In an earlier publication¹¹ we have described how manganese(II) bromide tetrahydrate reacted with cyclam in ethanol to form the characteristic olive-green colored bromide salt of the mixed valence complex

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for [Mn(cyclam)Br₂]Br (3).

| Atom | x | y | z | U(eq) ^a |
|-------|-----------|----------|---------|--------------------|
| Br(1) | 7285(1) | 2998(1) | 0 | 40(1) |
| Mn | 10000 | 5000 | 0 | 21(1) |
| Br(2) | 0 | 0 | 2500 | 37(1) |
| N | 10945(8) | 3552(7) | 1145(5) | 32(2) |
| C(1) | 12702(15) | 1808(15) | 0 | 49(4) |
| C(2) | 12625(9) | 2816(11) | 995(9) | 45(3) |
| C(3) | 10814(11) | 4549(11) | 2122(7) | 43(3) |

^aSee Table 2.Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for [Mn(cyclam)(NCS)₂]NCS (4).

| Atom | x | y | z | U(eq) ^a |
|-------|----------|----------|----------|--------------------|
| Mn(1) | -5000 | 5000 | 0 | 33(1) |
| N(1A) | -5985(3) | 5427(3) | 1028(3) | 40(1) |
| C(2A) | -6356(5) | 6525(4) | 846(3) | 52(2) |
| C(3A) | -5253(5) | 7091(3) | 556(3) | 48(2) |
| N(4A) | -4905(3) | 6544(3) | -269(2) | 41(1) |
| C(5A) | -3734(5) | 6942(4) | -568(4) | 51(2) |
| C(6A) | -3373(5) | 6349(4) | -1391(4) | 57(2) |
| C(7A) | -2948(4) | 5252(4) | -1170(3) | 53(2) |
| N(9A) | -3291(4) | 5095(3) | 1026(3) | 50(1) |
| C(9A) | -2634(5) | 5648(4) | 1513(3) | 44(2) |
| S(1A) | -1735(2) | 6450(1) | 2171(1) | 78(1) |
| Mn(2) | 0 | 0 | 0 | 34(1) |
| N(1B) | 1669(3) | 7(3) | -506(2) | 41(1) |
| C(2B) | 2669(4) | 13(4) | 316(3) | 52(2) |
| C(3B) | 2311(4) | -728(4) | 1029(4) | 50(2) |
| N(4B) | 1044(3) | -411(3) | 1243(3) | 40(1) |
| C(5B) | 494(5) | -1151(4) | 1849(3) | 50(2) |
| C(6B) | -787(5) | -811(4) | 2032(3) | 54(2) |
| C(7B) | -1818(5) | -830(4) | 1212(4) | 52(2) |
| N(9B) | 249(4) | 1600(3) | 398(3) | 52(2) |
| C(9B) | 38(4) | 2477(4) | 412(3) | 40(2) |
| S(1B) | -229(2) | 3694(1) | 425(1) | 76(1) |
| S(2) | 7091(1) | 1996(1) | 1588(1) | 61(1) |
| N(9) | 5211(5) | 574(5) | 1855(3) | 82(2) |
| C(9) | 5972(5) | 1165(5) | 1735(3) | 55(2) |

^aSee Table 2.

ion [Mn(cyclam)O]₂³⁺. We have now demonstrated that this dimeric compound reacts with hydrobromic acid within 24 h to form *trans*-[Mn(cyclam)Br₂]Br, and that *trans*-[Mn(cyclam)Cl₂]Cl·5H₂O and the interesting new nitrate complex, *trans*-[Mn(cyclam)(NO₃)₂]NO₃, can be synthesized by similar procedures starting from manganese(II) chloride tetrahydrate and manganese(II) nitrate, respectively. Unlike the other two compounds the chloro complex is formed from the dimeric compound within a few hours.

A treatment of the solid dimeric bromide with concentrated hydrobromic acid resulted in the formation of *cis*-[Mn(cyclam)Br₂]Br·H₂O, a compound that seems to represent the only *cis*-complex of this type that has been isolated so far. The compound is unstable in all solvents.

Description of the structures

[Mn(cyclam)(NO₃)₂]NO₃, (1). The manganese atom lies on a position of $\bar{1}$ (C_i) symmetry. The structure consists of centrosymmetric [Mn(cyclam)(NO₃)₂]⁺ cations which are linked by hydrogen bonds to the nitrate anions. A view of the cation is shown in Fig. 1, and the principal bond lengths and angles are presented in Table 6.

The geometry at manganese is *trans*-pseudo-octahedral, as predicted for related complexes from the spectroscopic investigations.^{6,7} The two independent Mn–N bond lengths are 2.031(4) and 2.041(4) Å; these values are shorter than those found for the corresponding (equatorial) bonds in the

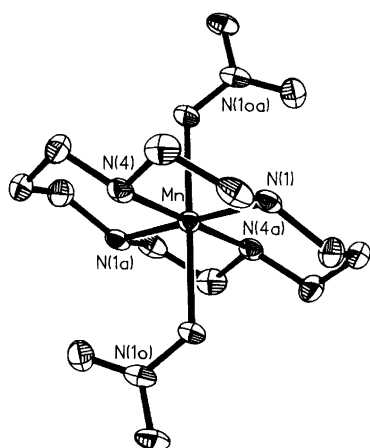


Fig. 1. View of the $[\text{Mn}(\text{cyclam})(\text{NO}_3)_2]^+$ cation in the crystal of the nitrate salt. Atoms labelled "a" are related to the parent atoms by inversion through the manganese. Carbon and oxygen atoms are unlabelled and hydrogen atoms are omitted for clarity.

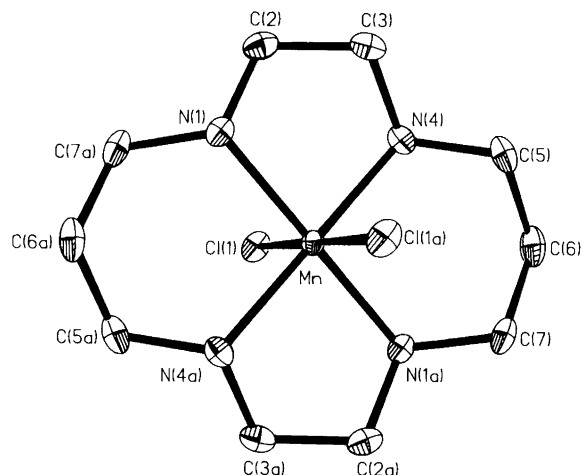


Fig. 2. View of the $[\text{Mn}(\text{cyclam})\text{Cl}_2]^+$ cation in the crystal of the nitrate salt. Atoms labelled "a" are related to the parent atoms by inversion through the manganese. Hydrogen atoms are omitted for clarity.

salts of $[\text{Mn}(\text{cyclam})\text{O}]_2^{3+}$,^{11,12} which is probably indicative of the *trans* effect of oxygen in the latter ion. The axial Mn–O bond length of 2.221(4) Å is very long, and is demonstrative of the axial elongation anticipated for this high-spin d^4 complex. The *cis* N–Mn–N bond angles are 84.8(2) and 95.2(2)°, with the smaller value being associated with the five-membered ring [N(1)–Mn–N(4)], as ex-

pected. In the di- μ -oxo complex, where the complex is necessarily *cis* rather than *trans*, the N(1)–Mn–N(4) angles are much smaller (ca. 80°), but this is due to the axial ligation of N(4) in that case.^{11,12}

The uncoordinated nitrate ion sits on a crystallographic C_2 axis which passes through N(20) and O(4). Each anion is linked to two different cations through N(4)–H(4)···O(4) hydrogen bonds, the N(4)···O(4) and H(4)···O(4) distances being 3.052 and 2.39 Å, while the N–H···O angle is 164°. It is improbable that this Mn–N(4)–H(4)···O(4)···H(4a)–N(4a)–Mn(a) interaction, involving seven atoms

Table 6. Bond lengths (in Å) and bond angles (in °) for $[\text{Mn}(\text{cyclam})(\text{NO}_3)_2]\text{NO}_3$ (1).

| | | | |
|------------------|----------|------------------|----------|
| Mn–N(1) | 2.041(4) | Mn–N(4) | 2.031(4) |
| Mn–O(1) | 2.221(4) | Mn–N(1A) | 2.041(4) |
| Mn–N(4A) | 2.031(4) | Mn–O(1A) | 2.221(4) |
| N(1)–C(2) | 1.486(6) | N(1)–C(7A) | 1.500(7) |
| C(2)–C(3) | 1.500(9) | C(3)–N(4) | 1.479(7) |
| N(4)–C(5) | 1.486(8) | C(5)–C(6) | 1.514(7) |
| C(6)–C(7) | 1.512(8) | C(7)–N(1A) | 1.500(7) |
| N(10)–O(1) | 1.278(6) | N(10)–O(2) | 1.237(6) |
| N(10)–O(3) | 1.232(6) | N(20)–O(4) | 1.263(8) |
| N(20)–O(5) | 1.234(6) | N(20)–O(5A) | 1.234(6) |
| N(1)–Mn–N(4) | 84.8(2) | N(1)–Mn–O(1) | 86.3(2) |
| N(4)–Mn–O(1) | 92.0(2) | N(1)–Mn–N(1A) | 180.0(1) |
| N(4)–Mn–N(1A) | 95.2(2) | O(1)–Mn–N(1A) | 93.7(2) |
| N(1)–Mn–N(4A) | 95.2(2) | N(4)–Mn–N(4A) | 180.0(1) |
| O(1)–Mn–N(4A) | 88.0(2) | N(1A)–Mn–N(4A) | 84.8(2) |
| N(1)–Mn–O(1A) | 93.7(2) | N(4)–Mn–O(1A) | 88.0(2) |
| O(1)–Mn–O(1A) | 180.0(1) | N(1A)–Mn–O(1A) | 86.3(2) |
| N(4A)–Mn–O(1A) | 92.0(2) | Mn–N(1)–C(2) | 107.2(3) |
| Mn–N(1)–C(7A) | 116.0(3) | C(2)–N(1)–C(7A) | 114.1(4) |
| N(1)–C(2)–C(3) | 108.3(4) | C(2)–C(3)–N(4) | 107.8(4) |
| Mn–N(4)–C(3) | 107.6(3) | Mn–N(4)–C(5) | 116.4(3) |
| C(3)–N(4)–C(5) | 112.1(4) | N(4)–C(5)–C(6) | 113.2(4) |
| C(5)–C(6)–C(7) | 114.9(5) | C(6)–C(7)–N(1A) | 112.2(5) |
| O(1)–N(10)–O(2) | 117.8(4) | O(1)–N(10)–O(3) | 119.9(4) |
| O(2)–N(10)–O(3) | 122.3(4) | Mn–O(1)–N(10) | 128.1(3) |
| O(4)–N(20)–O(5) | 119.2(3) | O(4)–N(20)–O(5A) | 119.2(3) |
| O(5)–N(20)–O(5A) | 121.7(7) | | |

Table 7. Bond lengths (in Å) and angles (in °) for $[\text{Mn}(\text{cyclam})\text{Cl}_2]\text{NO}_3$ (2).

| | | | |
|-----------------|------------|----------------|-----------|
| Mn–N(1) | 2.036(1) | Mn–N(4) | 2.033(1) |
| Mn–Cl(1) | 2.526(1) | Mn–N(1A) | 2.036(1) |
| N(1)–C(2) | 1.485(2) | N(1)–C(7A) | 1.484(2) |
| C(2)–C(3) | 1.506(3) | C(3)–N(4) | 1.490(3) |
| N(4)–C(5) | 1.483(2) | C(5)–C(6) | 1.518(3) |
| C(6)–C(7) | 1.511(3) | N–O(1) | 1.181(7) |
| N–O(2) | 1.440(7) | N–O(3) | 1.134(12) |
| N–O(11) | 1.296(29) | N–O(12) | 1.129(28) |
| N–O(13) | 1.360(112) | | |
| N(1)–Mn–N(4) | 85.5(1) | N(1)–Mn–Cl(1) | 92.3(1) |
| N(4)–Mn–Cl(1) | 88.7(1) | N(4)–Mn–N(1A) | 94.5(1) |
| Cl(1)–Mn–N(1A) | 87.7(1) | Cl(1)–Mn–N(4A) | 91.3(1) |
| Mn–N(1)–C(2) | 107.2(1) | Mn–N(1)–C(7A) | 117.0(1) |
| C(2)–N(1)–C(7A) | 113.7(1) | N(1)–C(2)–C(3) | 108.1(1) |
| C(2)–C(3)–N(4) | 108.0(2) | Mn–N(4)–C(3) | 106.6(1) |
| Mn–N(4)–C(5) | 117.2(1) | C(3)–N(4)–C(5) | 112.6(1) |
| N(4)–C(5)–C(6) | 112.6(2) | C(5)–C(6)–C(7) | 115.3(2) |
| C(6)–C(7)–N(1A) | 111.9(1) | O(1)–N–O(2) | 107.2(7) |
| O(1)–N–O(3) | 145.7(9) | O(2)–N–O(3) | 106.0(7) |
| O(1)–N–O(11) | 123.4(14) | O(1)–N–O(12) | 107.6(19) |
| O(11)–N–O(12) | 125.9(23) | O(2)–N–O(13) | 101.9(45) |
| O(3)–N–O(13) | 142.9(55) | | |

two hydrogen bonds, can provide a pathway for any appreciable magnetic interaction between the two metal centers. In addition to this interionic interaction there is intraionic hydrogen bonding in the cation between N(1) and terminal nitrate oxygen atom O(3), with N(1)⋯O(3) and H(1)⋯O(3) distances of 2.985 and 2.37 Å and an associated N–H⋯O angle of 145°.

[Mn(cyclam)Cl₂]NO₃, (2). Here again, the manganese atom lies on a position of $\bar{1}$ (*C_i*) symmetry. The structure of the cation is shown in Fig. 2, and the principal bond lengths and angles are listed in Table 7.

As in **1**, the complex is roughly *trans*-octahedral. The two independent Mn–N separations of 2.033(1) and 2.036(1) Å are consistent with the values in **1** (average value 2.036 Å), as are the *cis*-N–Mn–N bond angles of 85.5(1) and 94.5(1)°. The axial Mn–Cl separation of 2.526(1) Å is, as anticipated, very long.

The nitrogen atom of the nitrate ion lies on a crystallographic inversion center, which causes the anion to be disordered. This disorder occurs despite the existence of interionic hydrogen bonding between the nitrate ion and N(4) of the cation; as is seen in Fig. 3, either of the two disordered positions is capable of providing a suitably located oxygen atom for this hydrogen bond. The N⋯O(1), H⋯O(1) and N–H⋯O(1) metrical parameters are 2.886(7) Å, 2.19 Å and 142°, while those associated with O(2a) are 2.947(8) Å, 2.21 Å, and 148°. In addition to this interaction there is significant hydrogen bonding between neighboring cations, involving N(1)–H(1) of one cation and a chloride ion on the adjacent cation. These interactions, which are depicted in Fig. 4, lead to a chain structure running parallel to the crystallographic *a*-axis, in which each cation is linked to its neighbors above and below by pairs of centrosymmetric N–H⋯Cl hydrogen bonds. The N(1)⋯Cl(1) and

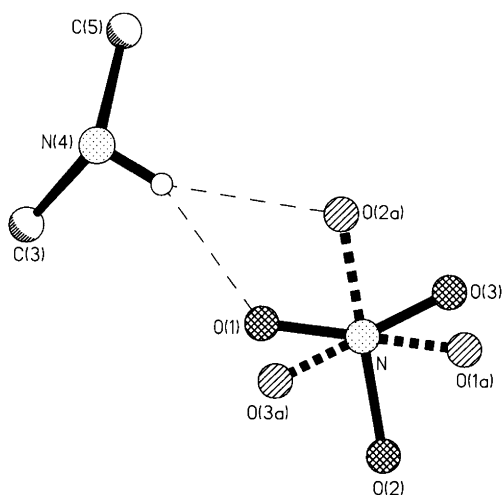


Fig. 3. The hydrogen bonding between the cation [N(4)–H] and the disordered nitrate anion in [Mn(cyclam)Cl₂]NO₃. Atoms O(1), O(2) and O(3) [cross-hatched] represent one of the disordered sets of oxygen positions, while those labelled O(1a), O(2a) and O(3a) [striped] represent the other disordered set of positions.

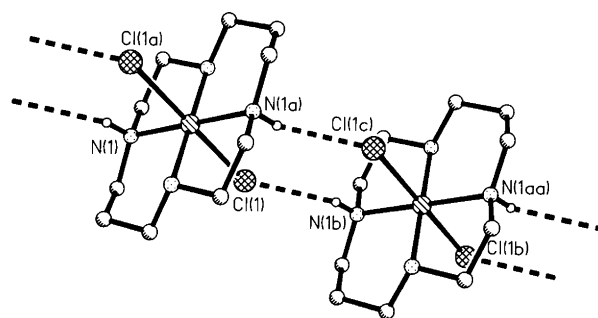


Fig. 4. The hydrogen bonding between neighboring [Mn(cyclam)Cl₂]⁺ cations in the crystal of the nitrate salt. This interaction may be magnetically significant (see text and Fig. 7).

H(1)⋯Cl(1) distances and N–H⋯Cl angle are 3.246(3) Å, 2.55 Å and 146°, respectively, while the Mn⋯Mn separation is 6.547 Å [i.e. the *a*-axis length]. It is possible that these Mn–N(1)–H(1)⋯Cl(1)–Mn interactions, which involve only five atoms and one hydrogen bond, might provide a significant magnetic pathway in the crystals (*vide infra*).

[Mn(cyclam)Br₂]Br, (3). With only two manganese atoms in space group *P4₂/m*, the cation is required to have crystallographic *2/m* (*C_{2h}*) symmetry. The structure of the complex consists of these centrosymmetric cations and bromide anions, which are linked by hydrogen-bonding interactions. A view of the cation is given in Fig. 5, and the principal bond lengths and angles are presented in Table 8.

The geometry about each manganese center is again roughly *trans* octahedral, the nitrogen atoms of the cyclam ligand occupying four *cis* sites with the coordinated bromide ligands *trans* axially located. The crystallographic *C₂*

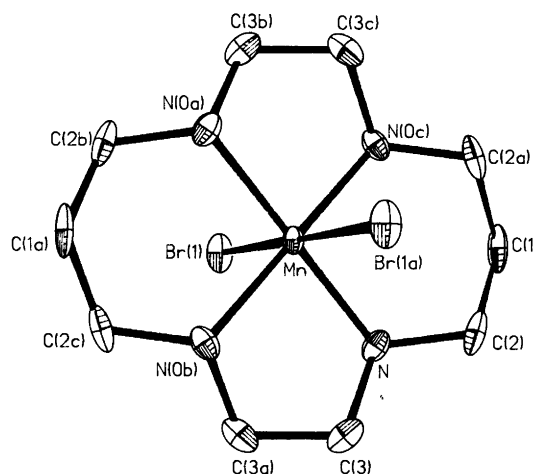


Fig. 5. View of the [Mn(cyclam)Br₂]⁺ cation in the crystal of the bromide salt. The site symmetry at manganese is *C_{2h}*, with the mirror plane passing through atoms labelled Br(1), Br(1a), C(1), C(1a) and Mn and the *C₂* axis passing through Br(1), Br(1a) and Mn. Atoms labelled "a", "b" or "c" are related to the parent atoms by either reflection or rotation relative to one of these two symmetry operations. Hydrogen atoms are omitted for clarity.

Table 8. Bond lengths (in Å) and angles (in °) for [Mn(cyclam)Br₂]Br (3).

| | | | |
|-----------------|-----------|-----------------|-----------|
| Br(1)–Mn | 2.689(1) | Mn–N | 2.029(6) |
| Mn–Br(1A) | 2.689(1) | Mn–NA | 2.029(6) |
| Mn–NB | 2.029(6) | Mn–NC | 2.029(6) |
| N–C(2) | 1.475(10) | N–C(3) | 1.502(11) |
| C(1)–C(2) | 1.524(13) | C(1)–C(2A) | 1.524(13) |
| C(3)–C(3A) | 1.484(18) | | |
| Br(1)–Mn–N | 87.8(2) | Br(1)–Mn–Br(1A) | 180.0(1) |
| N–Mn–Br(1A) | 92.2(2) | Br(1)–Mn–NA | 92.2(2) |
| N–Mn–NA | 180.0(1) | Br(1A)–Mn–NA | 87.8(2) |
| Br(1)–Mn–NB | 92.2(2) | N–Mn–NB | 85.6(3) |
| Br(1A)–Mn–NB | 87.8(2) | NA–Mn–NB | 94.4(3) |
| Br(1)–Mn–NC | 87.8(2) | N–Mn–NC | 94.4(3) |
| Br(1A)–Mn–NC | 92.2(2) | NA–Mn–NC | 85.6(3) |
| NB–Mn–NC | 180.0(1) | Mn–N–C(2) | 117.8(6) |
| Mn–N–C(3) | 107.1(5) | C(2)–N–C(3) | 112.7(7) |
| C(2)–C(1)–C(2A) | 116.2(11) | N–C(2)–C(1) | 111.0(8) |
| N–C(3)–C(3A) | 108.5(5) | | |

axis passes through the middle of the bonds labelled C(3)–C(3a) and C(3b)–C(3c) in Fig. 5, i.e. the two ethylene linkages C(1)–C(3) and C(9)–C(10) in the standard numbering scheme for cyclam. Atoms C(1) and C(1a) [normally C(6) and C(13)] and the coordinated bromides, Br(1) and Br(1a), lie on the mirror plane which is perpendicular to the C₂ axis. Hence there is only one independent Mn–N distance [2.029(6) Å] and one independent Mn–Br distance [2.689(1) Å] in the cation. This Mn–N distance can be compared to those described above for **1** [average 2.036(7) Å] and **2** [average 2.034(2) Å]. The Mn–Br axial bond is very long, and can be readily compared to the Mn–Cl distance in **2**. The values of 2.689(1) Å for Mn–Br in **3** and 2.526(1) Å for Mn–Cl in **2** differ by 0.163(1) Å, which is similar to the difference between the covalent radii of Br and Cl [estimated as 0.15 Å by Pauling¹³].

The *cis* bond angles subtended by the ligand at manganese are 85.6(3) and 94.4(3)°, with the smaller value being subtended by the nitrogen atoms separated by two carbon atoms, as expected. These angles are again comparable to those observed in **1** and **2**, above.

The ionic bromide ion Br(2) sits on a position of site symmetry 4 (S₄), and each Br(2) ion is hydrogen bonded to four different N–H groups from four different cations. Alternatively, each cation is hydrogen bonded to four different Br(2) anions. The N···Br and H···Br distances are 3.410 and 2.73 Å, respectively, and the associated N–H···Br angle is 135.2°. This N···Br separation can be compared to those of 3.45 to 3.47 Å reported in the various forms of ammonium bromide, the classical example of N–H···Br hydrogen bonding; similar values are observed in the bromide salt of the di-μ-oxo complex [Mn(cyclam)O]₂³⁺.¹¹ Shorter H···Br separations of 2.57 to 2.72 Å have been attributed to N–H···Br hydrogen bonding in [Cr(en)₂OH]₂Br₄·2H₂O.¹⁴

[Mn(cyclam)(NCS)₂]/NCS, (**4**). With four molecules in P2₁/c, no crystallographic symmetry need be imposed on the cations. Actually, however, the complex crystallizes

with two independent cations in the cell, each of which is therefore constrained to lie on an inversion center. A view of one cation is shown in Fig. 6, and the bond lengths and angles in the complex are listed in Table 9.

The geometries of the two independent cations are essentially similar. The four equatorial Mn–N bond lengths are in the range 2.032(4) to 2.043(4) Å, with an average of 2.038(5) Å; obviously, these distances are entirely consistent with those in **1**, **2** and **3**. The axial Mn–N (isothiocyanate) bonds are 2.154(4) and 2.178(4) Å in the two cations, demonstrating an axial elongation of approximately 0.13 Å. The ligand N–Mn–N angles are 85.4(2) and 94.6(2)° in one cation and 85.5(1) and 94.5(1)° in the other, in agreement with the observations above.

The principal difference between the two cations is in the orientations of the coordinated NCS[−] ligand. In the cation shown in Fig. 6, the Mn–N–C angle is 158.4(4)°, while in the other cation it is only 144.6(4)°. Both of these are within the range observed for other complexes,^{15,16} but the latter value is at the lower end of the observed range. The reason for this difference may be explained by the hydrogen bonding interactions in the crystal (*vide infra*). The coordinated isothiocyanate ligands are linear [N–C–S angles 178.2(4) and 178.9(4)°], with N–C bond lengths of 1.159(6) and 1.163(6) Å and C–S separations of 1.602(5) and 1.620(5) Å. In the uncoordinated anion, the corresponding values are 178.4(5)°, 1.154(8) Å and 1.653(6) Å. The C–S bond lengths here are worthy of some discussion. In ionic KNCS, the C–S bond of 1.689(13) Å is very long,^{15,16} which may indicate that in the free anion we may expect a longer C–S bond than in the coordinated species. In several earlier structures, no significant difference was noted between the geometries of coordinated and uncoor-

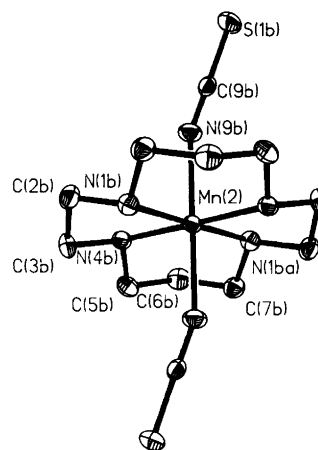


Fig. 6. View of one of the two crystallographically independent [Mn(cyclam)(NCS)₂]⁺ cations in the crystal of the thiocyanate salt. The site symmetry at manganese is C_i, and atoms labelled "a" are related to the parent atoms by inversion through the manganese. Hydrogen atoms are omitted for clarity. The other cation is substantially similar to this one, although the Mn–N(9)–C(9) angles in the two cations are significantly different (see text).

Table 9. Bond lengths (in Å) and angles (in °) for [Mn(cyclam)(NCS)₂]NCS (**4**).

| | | | |
|---------------------|----------|---------------------|----------|
| Mn(1)–N(1A) | 2.032(4) | Mn(1)–N(4A) | 2.041(4) |
| Mn(1)–N(9A) | 2.178(4) | Mn(1)–N(1AA) | 2.032(4) |
| Mn(1)–N(4AA) | 2.041(4) | Mn(1)–N(9AA) | 2.178(4) |
| N(1A)–C(2A) | 1.489(6) | N(1A)–C(7AA) | 1.486(6) |
| C(2A)–C(3A) | 1.509(8) | C(3A)–N(4A) | 1.483(6) |
| N(4A)–C(5A) | 1.488(7) | C(5A)–C(6A) | 1.516(8) |
| C(6A)–C(7A) | 1.510(7) | C(7A)–N(1AA) | 1.486(6) |
| N(9A)–C(9A) | 1.163(6) | C(9A)–S(1A) | 1.620(5) |
| Mn(2)–N(1B) | 2.043(4) | Mn(2)–N(4B) | 2.034(3) |
| Mn(2)–N(9B) | 2.154(4) | Mn(2)–N(1BA) | 2.043(4) |
| Mn(2)–N(4BA) | 2.034(3) | Mn(2)–N(9BA) | 2.154(4) |
| N(1B)–C(2B) | 1.472(5) | N(1B)–C(7BA) | 1.500(6) |
| C(2B)–C(3B) | 1.501(7) | C(3B)–N(4B) | 1.502(6) |
| N(4B)–C(5B) | 1.482(6) | C(5B)–C(6B) | 1.510(8) |
| C(6B)–C(7B) | 1.491(7) | C(7B)–N(1BA) | 1.500(6) |
| N(9B)–C(9B) | 1.159(6) | C(9B)–C(1B) | 1.602(5) |
| S(2)–C(9) | 1.653(6) | N(9)–C(9) | 1.154(8) |
| | | | |
| N(1A)–Mn(1)–N(4A) | 85.4(2) | N(1A)–Mn(1)–N(9A) | 88.3(1) |
| N(4A)–Mn(1)–N(9A) | 90.7(2) | N(1A)–Mn(1)–N(1AA) | 180.0(1) |
| N(4A)–Mn(1)–N(1AA) | 94.6(2) | N(9A)–Mn(1)–N(1AA) | 91.7(1) |
| N(1A)–Mn(1)–N(4AA) | 94.6(2) | N(4A)–Mn(1)–N(4AA) | 180.0(1) |
| N(9A)–Mn(1)–N(4AA) | 89.3(2) | N(1AA)–Mn(1)–N(4AA) | 85.4(2) |
| N(1A)–Mn(1)–N(9AA) | 91.7(1) | N(4A)–Mn(1)–N(9AA) | 89.3(2) |
| N(9A)–Mn(1)–N(9AA) | 180.0(1) | N(1AA)–Mn(1)–N(9AA) | 88.3(1) |
| N(4AA)–Mn(1)–N(9AA) | 90.7(2) | Mn(1)–N(1A)–C(2A) | 106.6(3) |
| Mn(1)–N(1A)–C(7AA) | 116.3(3) | C(2A)–N(1A)–C(7AA) | 113.4(4) |
| N(1A)–C(2A)–C(3A) | 108.2(4) | C(2A)–C(3A)–N(4A) | 107.4(4) |
| Mn(1)–N(4A)–C(3A) | 106.7(3) | Mn(1)–N(4A)–C(5A) | 117.6(3) |
| C(3A)–N(4A)–C(5A) | 113.6(4) | N(4A)–C(5A)–C(6A) | 112.7(4) |
| C(5A)–C(6A)–C(7A) | 114.6(4) | C(6A)–C(7A)–N(1AA) | 111.7(4) |
| Mn(1)–N(9A)–C(9A) | 144.6(4) | N(9A)–C(9A)–S(1A) | 178.2(4) |
| N(1B)–Mn(2)–N(4B) | 85.5(1) | N(1B)–Mn(2)–N(9B) | 90.7(2) |
| N(4B)–Mn(2)–N(9B) | 89.3(1) | N(1B)–Mn(2)–N(1BA) | 180.0(1) |
| N(4B)–Mn(2)–N(1BA) | 94.5(1) | N(9B)–Mn(2)–N(1BA) | 89.3(2) |
| N(1B)–Mn(2)–N(4BA) | 94.5(1) | N(4B)–Mn(2)–N(4BA) | 180.0(1) |
| N(9B)–Mn(2)–N(4BA) | 90.7(1) | N(1BA)–Mn(2)–N(4BA) | 85.5(1) |
| N(1B)–Mn(2)–N(9BA) | 89.3(2) | N(4B)–Mn(2)–N(9BA) | 90.7(1) |
| N(9B)–Mn(2)–N(9BA) | 180.0(1) | N(1BA)–Mn(2)–N(9BA) | 90.7(2) |
| N(4BA)–Mn(2)–N(9BA) | 89.3(1) | Mn(2)–N(1B)–C(2B) | 106.6(3) |
| Mn(2)–N(1B)–C(7BA) | 116.1(3) | C(2B)–N(1B)–C(7BA) | 113.7(4) |
| N(1B)–C(2B)–C(3B) | 108.4(4) | C(2B)–C(3B)–N(4B) | 107.8(4) |
| Mn(2)–N(4B)–C(3B) | 106.5(3) | Mn(2)–N(4B)–C(5B) | 118.2(3) |
| C(3B)–N(4B)–C(5B) | 113.8(4) | N(4B)–C(5B)–C(6B) | 112.0(4) |
| C(5B)–C(6B)–C(7B) | 116.3(4) | C(6B)–C(7B)–N(1BA) | 112.5(4) |
| Mn(2)–N(9B)–C(9B) | 158.4(4) | N(9B)–C(9B)–S(1B) | 178.9(4) |
| S(2)–C(9)–N(9) | 178.4(5) | | |

minated NCS[−] ions,^{16,17} and it is apparent from other precise studies that values as low as 1.61 and as high as 1.648(4) Å are “normal” for N-bond coordinated thiocyanate,^{18–20} and a value of 1.663(7) Å has been observed for the N-bound species.²¹ Nonetheless, the distance of 1.653(6) Å observed for the uncoordinated species here is among the highest recorded to date, and is clearly longer than those in the coordinated ions in the same crystal.

There are four examples of hydrogen bonding in the crystals of **4**. The first is an interaction between the two independent cations formed by N(4)–H \cdots S interactions involving the cyclam ligands on Mn(2) and the thiocyanate on Mn(1). This leads to a chain-like structure of

Mn(2) \cdots Mn(1) \cdots Mn(2) \cdots Mn(1) centers in the crystal. The N(4b)–H(4b) \cdots S(1a) metrical parameters are 3.326 Å (N \cdots S), 2.43 Å (H \cdots S) and 165° (N–H \cdots S). The resulting Mn(2)–N(4b)–H(4b) \cdots S(1a)–C(9a)–N(9a)–Mn(1) interaction involves seven atoms, and is evidently not magnetically significant in this system. The other hydrogen-bonding interactions involve the uncoordinated thiocyanate anion, whose S atom forms hydrogen bonds to N(4)–H of Mn(1) and N(1)–H of Mn(2), leading to Mn(1)–N(4)–H \cdots S \cdots H–N(1)–Mn(2) systems. In addition, the nitrogen atom of the NCS[−] anion forms a hydrogen bond to N(1)–H of a different Mn(1) center. The metrical parameters involved are 3.368 Å [N(4) \cdots S], 2.56 Å [H(4) \cdots S], 147° [N(4)–

Table 10. Chemically equivalent bond lengths (in Å) in the cyclam ligands.

| Atoms | 1 | 2 | 3 | 4 |
|-------------------|-------|-------|-------|-------|
| N(1)–C(2) | 1.486 | 1.485 | 1.502 | 1.489 |
| N(4)–C(3) | 1.479 | 1.490 | 1.502 | 1.483 |
| N(8)–C(9) | 1.486 | 1.490 | 1.502 | 1.472 |
| N(11)–C(10) | 1.479 | 1.485 | 1.502 | 1.502 |
| Average: 1.490(9) | | | | |
| N(1)–C(14) | 1.500 | 1.484 | 1.475 | 1.486 |
| N(4)–C(5) | 1.486 | 1.483 | 1.475 | 1.488 |
| N(8)–C(7) | 1.500 | 1.484 | 1.475 | 1.500 |
| N(11)–C(12) | 1.486 | 1.483 | 1.475 | 1.482 |
| Average: 1.485(9) | | | | |
| C(2)–C(3) | 1.500 | 1.506 | 1.484 | 1.509 |
| C(9)–C(10) | 1.500 | 1.506 | 1.484 | 1.501 |
| Average: 1.499(9) | | | | |
| C(5)–C(6) | 1.514 | 1.518 | 1.524 | 1.516 |
| C(6)–C(7) | 1.512 | 1.511 | 1.524 | 1.510 |
| C(12)–C(13) | 1.514 | 1.518 | 1.524 | 1.510 |
| C(13)–C(14) | 1.512 | 1.511 | 1.524 | 1.491 |
| Average: 1.515(8) | | | | |

H(4)⋯S], 3.405 Å [N(1b)⋯S], 2.56 Å [H(1b)⋯S], 152° [N(1b)–H(1b)⋯S], 3.046 Å [N(1)⋯N(9)], 2.29 Å [H(1)⋯N(9)], and 143° [N(1)–H(1)⋯N(9)].

The cyclam ligand. The four structures above allow a reasonably precise description of the bond lengths in the ligand. Using the normal IUPAC numbering scheme, we may deduce that the weighted averages for chemically equivalent bond lengths in coordinated cyclam in these four studies are as given in Table 10. There are only four chemically distinct bonds in the ligand. These are N(1)–C(2) [≡ N(4)–C(3), N(8)–C(9), N(11)–C(10)], with an average value of 1.490(9) Å; N(1)–C(14) [≡ N(4)–C(5), N(8)–C(7), N(11)–C(12)], average 1.485(9) Å; C(2)–C(3) [≡ C(9)–C(10)], average 1.499(9) Å; and C(5)–C(6) [≡ C(6)–C(7), C(12)–C(13), C(13)–C(14)], average 1.515(8) Å.

Magnetic properties. The magnetic properties of the complexes, as well as related complexes described by earlier workers,^{6,7} are consistent with their formulation as high-spin d^4 Mn(III) complexes, except for the *trans*-dicyano compound, which is a low-spin d^4 Mn(III) complex.

All the high-spin complexes have effective magnetic moments near the expected value of 4.9 μ_B , and the observed moments are independent of temperature in the approximate range 50–300 K, as predicted for monomeric species. At lower temperatures the effective magnetic moments increase and show a maximum at approximately 6 K. This can be interpreted as an intermolecular ferromagnetic interaction in the solid state or as a reorientation of the crystals in the magnetic field, because the susceptibility of the crystals could be very anisotropic. To settle this

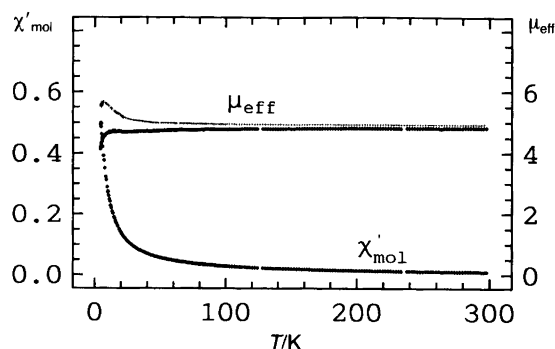


Fig. 7. The temperature dependence of the magnetic susceptibility and effective magnetic moment of a sample of [Mn(cyclam)(NO₃)₂]NO₃ mixed with 10% vacuum grease. The grease effectively prevents the orientation of the anisotropic crystals in the magnetic field. The curve (+++) represents the effective magnetic moment of the same sample measured without grease.

question the susceptibility was measured of *trans*-[Mn(cyclam)(NO₃)₂]NO₃ mixed with 10% silicone vacuum grease. The results are shown in Fig. 7, which definitely shows we are dealing with very anisotropic crystals, because the maximum on the magnetic moment curve disappears when the grease prevents reorientation of the crystals.

The anisotropy of the manganese(III) crystals presumably arises because of a considerable zero-field splitting (ZFS). We have been unable to determine the ZFS either from the susceptibility measurements or from EPR spectra. Frozen glasses of the complexes dissolved in *N*-methylformamide show no X-band EPR spectra in the temperature range 4–200 K.

The magnetic susceptibility and effective magnetic moment data for [Mn(cyclam)Cl₂]NO₃, which are shown in Fig. 8, are anomalous in that the susceptibility shows a maximum near 6 K and the moment exhibits a steep decline with decreasing temperature. This maximum was confirmed by a repeated measurement on another sample.

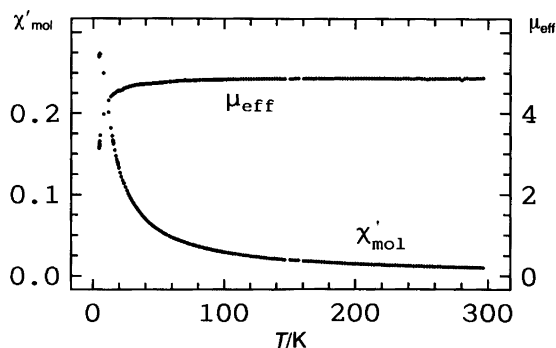


Fig. 8. The temperature dependence of the magnetic susceptibility and effective magnetic moment of a powdered sample of [Mn(cyclam)Cl₂]NO₃. The maximum observed in the susceptibility curve and the decline in effective magnetic moment with decreasing temperature are attributed to the intermolecular interaction shown in Fig. 4 (see text).

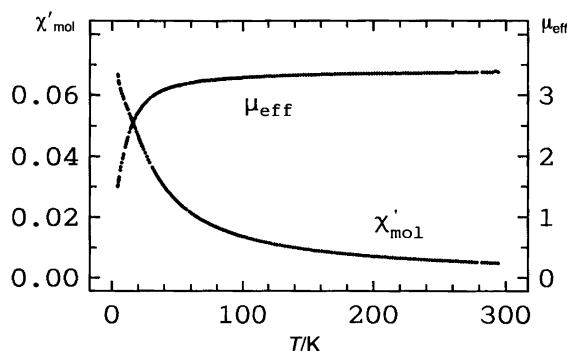


Fig. 9. The temperature dependence of the magnetic susceptibility and the effective magnetic moment of a sample of *trans*-[Mn(cyclam)(CN)₂]ClO₄.

This susceptibility behavior cannot be explained by zero-field splitting, and must be the result of some weak intermolecular antiferromagnetic interaction; we have found no suitable model for the description of an infinite chain of Mn(III) centers, but the exchange interaction must be of the order of 1 cm⁻¹. It is noteworthy that, as shown in Fig. 4, there is a potentially significant magnetic pathway in this complex which is not present in the other complexes whose crystal structures have been examined (*vide supra*).

In Fig. 9 is shown the susceptibility of *trans*-[Mn(cyclam)(CN)₂]ClO₄. A magnetic moment of 3.37 μ_B at room temperature compared with 4.9 μ_B for the other complexes shows that we have one of the rare cases of a low-spin d⁴ Mn(III) complex. The magnetic moments have been reported²² for K₃[Mn(CN)₆], another low-spin Mn(III) compound, to be in the range 2.95–3.60 μ_B, which compares well with our findings.

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