Synthesis and Characterization of Tris(2-pyridylmethylamine)-manganese(II) Perchlorate and its Zinc(II) Analogue

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The synthesis and structural characterization of the complex tris(2-pyridylmethylamine)manganese(II) perchlorate, $[Mn(C_6H_8N_2)_3](ClO_4)_2$, are described. The complex crystallized in the space group $P\bar{4}3n$ of the cubic system with $a = 17.137$ (2) Å and $Z = 8$; $D_x = 1.525$ g cm^{-1}. The structure has been refined by full matrix least-squares techniques to a final R-factor of 0.033 based on 582 observed unique intensities collected with Mo $K\alpha$ radiation, $\mu = 7.7$ cm^{-1}. The cation crystallizes as the *fac* isomer, and exhibits crystallographic three-fold symmetry. The Mn–N(py) and Mn–N(amine) bond lengths are equal (2.266 Å), and the chelate bite angle is 74.8 (2)°. The magnetic susceptibility in the temperature range 4–300 K corresponds to $\mu_{eff} = 5.92$, indicating high-spin Mn(II) ($S = 5/2$). The EPR spectrum of the complex doped into the isomorphous zinc host shows the expected six-line pattern, with $g = 2.00$ and $A = 79.0 \times 10^{-4}$ cm^{-1}.

There is continued interest in the properties of transition metal complexes of the general type $[M(chel)_3]^{n+}$, where chel represents a nonsymmetric bidentate ligand. Of particular importance has been the tris(2-picolylamine)iron(II) system, which is a classical example of a spin-crossover system.[1] As a result of this interest, the structures of many salts of both isomers of this iron(II) complex have been determined,[1-3] and more recently, the structure of a solvated form of the *mer* isomer of the zinc(II) analogue was also reported.[4] Our own interest is in the chemistry of manganese, and it is surprising to note that very few complexes of manganese(II) of the type $[Mn(chel)_3]^{2+}$ have been structurally characterized, the most germane example being the structure of the bromide salt of tris(2-(dimethylamino)ethyl)aminemanganese(II), $[Mn(daea)_3]^{2+}$.[5] We report here the synthesis of the tris complexes of manganese(II) and zinc(II) with 2-picolylamine from aqueous solution, and the structural and electron paramagnetic characterization of the perchlorate salt of the manganese complex, $[Mn(pico)_3](ClO_4)_2$, where pico = $C_8H_8N_2$. The synthesis of this complex from ethanolic solution has been reported by Sutton.[6]

Experimental

Reagents. 2-Picolylamine was purchased from Fluka AG, Buchs, Switzerland. All other chemicals were of reagent grade and were used without further purification.

Analyses. The manganese and zinc analyses were performed on a Perkin-Elmer 403 atomic absorption spectrophotometer. The carbon, nitrogen and hydrogen analyses were performed at the microanalytical laboratory of the H. C. Ørsted Institute using standard methods.

EPR spectra. EPR spectra were recorded at liquid helium temperature on a Bruker ESP 300 spectrometer operating at a frequency of 9.38 GHz (X-band) with magnetic field modulation of 100 kHz, modulation amplitude of 7 G, and microwave power of 10 mW. Samples were examined as frozen glasses in *N*-methylformamide solution and as solid solutions in the zinc analogue.

Magnetic susceptibilities. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 4–300 K at field of 1.3 T. A description of the equipment has appeared elsewhere.[7]

Syntheses. Tris(2-pyridylmethylamine)manganese(II) perchlorate, $[Mn(C_6H_8N_2)_3](ClO_4)_2$. 2-Picolylamine (1.6 ml, ≈ 16 mmol) was dissolved in water (4 ml), and the pH of the solution was adjusted to 9.0 by means of hydrochloric acid (4 M). An aqueous solution of $Mn(SO_4) \cdot H_2O$ (680 mg, ≈ 4.0 mmol in 3 ml) was added, and nitrogen gas was bubbled through the solution for 10 min. The resulting solution was allowed to sit in a stoppered flask for 6 h, when a saturated solution of sodium perchlorate (~ 1 ml) was added dropwise very slowly. The whitish crystals that separated were washed with aqueous sodium perchlorate (1 M) and with ethanol (96 %). Yield 1.64 g (71 %) of very pure crystals. Anal. Found: C, 37.22; H, 4.15; N, 14.47; Cl,

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12.32; Mn, 9.49. Calc. for $C_{18}H_{24}N_6Cl_2O_8Mn$: C, 37.39; H, 4.18; N, 14.53; Cl, 12.36; Mn, 9.50. The complex could be recrystallized from water with a loss of approximately one third of the product and no apparent gain in purity. Very large crystals were obtained when the aqueous sodium perchlorate was added until the onset of cloudiness in the solution. After 24 h, very large, pale yellow crystals separated out.

Tris(2-pyridylmethylamine)zinc(II) perchlorate, $[Zn(C_6H_8N_2)_3](ClO_4)_2$. The complex was prepared as above, but from zinc nitrate hexahydrate (700 mg, ≈2.35 mmol). Yield: 1.12 g (84%). Anal. Found: C, 36.81; H, 3.99; N, 14.31; Cl, 12.05; Zn, 11.46. Calc. for $C_{18}H_{24}N_6Cl_2O_8Zn$: C, 36.72; H, 4.11; N, 14.27; Cl, 11.38; Zn, 11.10. The complex could be recrystallized from boiling water to give large shiny crystals with a loss of approximately 40% of the product. Compounds containing small amounts of manganese doped in the zinc host could be obtained by substituting manganese(II) sulfate monohydrate for appropriate amounts of zinc(II) nitrate hexahydrate.

Crystal structure determination. The crystal structure of the perchlorate salt of the manganese complex was determined at 21 °C on a Nicolet R3m/V diffractometer equipped with Mo $K\alpha$ radiation ($\lambda\ K\alpha_1 = 0.709\,26$ Å; $\lambda\ K\alpha_2 = 0.713\,54$ Å) and a graphite monochromator. The crystal system was shown to be cubic by examination of axial photographs, and the unit cell constant was determined by least-squares refinement of the angular settings of 25 intense data in the region $20 < 2\theta(\text{Mo}) < 25°$. Systematic absences of $(hk\ell)$ for $\ell = 2n+1$ are consistent with space groups $Pm3n$ (No. 223) and $P\bar{4}3n$ (No. 218). With eight molecules in the unit cell, the manganese centers would be constrained to 32 (D_3) symmetry in $Pm3n$; such symmetry is impossible for any isomer of a complex with three unsymmetrical bidentate ligands. In $P\bar{4}3n$, however, manganese is constrained only to three (C_3) symmetry, which is possible for the *facial* isomer. Hence, the space group was deduced to be $P\bar{4}3n$, and this assignment was confirmed by the eventual structure refinement.

The intensities of three standard reflections were monitored at the beginning and end of the data collection, and also after every 100 data. The standard reflections were (600), (060) and (006), and their intensities showed a maximum deviation of less than 3.0%. An empirical absorption correction was applied to the intensity data. Other experimental details and the cell constant are collected in Table 1. The zinc analogue was shown to be isomorphous with the manganese complex by examination of powder patterns. The manganese structure was solved by direct methods and refined by full-matrix least-squares techniques on *F*. The programs used were from the SHELXTL system.[8] The weighting scheme was as described by Ibers and coworkers,[9] the value of whose weighting factor *p* refined to 0.0049. Hydrogen atoms were placed in calculated positions (C–H = 0.96 Å), while other atoms were refined anisotropically. The absolute configuration of the complex was determined using an η refinement as described by Rogers.[10] In the final least-squares cycle, no parameter shifted by more than 0.20σ, indicating that the refinement had converged. Final values of the agreement factors are

Table 1. Crystallographic and data collection parameters.

Formula	$MnC_{18}H_{24}N_6O_8Cl_2$
Colour and habit	Yellow cube
Crystal dimensions	0.30×0.30×0.30 mm
System	Cubic
Space group	$P\bar{4}3n$
Cell dimensions	$a = 17.137(2)$ Å
Volume	5032.7(9) Å^3
Observed density	1.525(10) g cm^{-3}
Z	8
Calculated density	1.537 g cm^{-3}
F(000)	2376
Absorption coefficient	0.77 mm^{-1}
Transmission coefficients	0.514–0.572
Index ranges	$0 \le h \le 22$
	$0 \le k \le 22$
	$0 \le \ell \le 22$
Scan range	$3 < 2\theta(\text{Mo}) < 55°$
Scan type	2θ scans
Scan width	$2(0.6 + 0.35\tan\theta)$
No. of reflections measured	3331
No. of unique reflections, R_{int}	984, 0.0170
Observed independent reflections	582 [$I > 3\sigma(I)$]
R	0.0331
wR	0.0538
S (= goodness of fit)	0.757
Max. and min. peaks in difference Fourier	+0.29, −0.30 e Å^{-3}

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (10^3 Å^2).

Atom	*x*	*y*	*z*	*U*(eq)[a]	SOF[b]
Mn	1597(1)	1597(1)	1597(1)	47(1)	1/3
N(1)	2535(3)	2338(3)	1032(3)	55(2)	
C(2)	2924(4)	1998(5)	447(4)	68(2)	
C(3)	3386(5)	2420(7)	−34(5)	100(3)	
C(4)	3457(6)	3202(7)	59(6)	117(4)	
C(5)	3072(5)	3555(5)	659(6)	99(3)	
C(6)	2602(4)	3110(4)	1133(5)	73(2)	
C(7)	2842(4)	1129(5)	373(5)	83(3)	
N(2)	2092(4)	850(3)	625(3)	67(2)	
Cl(1)	8459(1)	−8459(1)	−8459(1)	62(1)	1/3
O(11)	9169(4)	−8600(5)	−8076(4)	114(3)	
O(12)	7991(4)	−7991(4)	−7991(4)	141(3)	1/3
Cl(2)	0	0	0	43(1)	1/12
O(21)	−435(10)	435(10)	435(10)	263(7)	1/6
O(22)	453(10)	453(10)	453(10)	206(7)	1/6
Cl(3)	0	5000	0	89(2)	1/4
O(31)	30(27)	5561(12)	−468(17)	132(7)	1/4
O(32)	−690(9)	5542(9)	14(9)	135(5)	1/2
O(33)	0	5000	827(10)	122(6)	1/4

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Site occupancy factor. Atoms with no entry have a SOF of 1.0, which leads to 24 atoms per cell.

$R = 0.0331$ and $wR = 0.0538$, based on 582 independent intensities with $I > 3\sigma(I)$. Atomic scattering factors and anomalous dispersion corrections were from the tabulations in the SHELXTL program system.[8] The positional parameters of the non-hydrogen atoms are presented in Table 2.*

Results and discussion

The crystals of the manganese complex consist of $[Mn(pico)_3]^{2+}$ cations and perchlorate anions. A view of the cation is given in Fig. 1, and selected bond lengths and angles in the cation are listed in Tables 3 and 4, respectively.

With eight molecules in the cubic space group $P\bar{4}3n$ (No. 218), the manganese atoms are required to have C_3 symmetry. Consequently, as can be seen in Fig. 1, the isomer crystallized here is the *fac* isomer, since the highest symmetry this isomer can exhibit is C_3, while the *mer* isomer cannot exhibit three-fold symmetry. Hence, both the manganese and zinc complexes reported here are *fac* isomers, and are the first reported complexes of the type $[M(pico)_3]^{2+}$ to exhibit rigorous crystallographic three-fold symmetry. The isomer shown in Fig. 1 exhibits the Δ configuration at the manganese(II) center. The conformation of the ligands is δ, all three ligands having the same conformation as a consequence of the three-fold symmetry, so the isomer depicted here is the Δδδδ isomer. The Mn–N (pyridine) bonds of 2.266(5) Å are indistinguishable in length from those of 2.266(6) Å to the amine nitrogen atoms; this is in contrast to the *fac* isomer of the iron(II) analogue, in which the Fe–N(py) bonds are significantly shorter than the Fe–N(amine) bonds.[1] In the high-spin *mer* isomers of the iron(II) complex and in the *mer* isomer of the zinc complex, however, the M–N(py) bonds are longer than the M–N(amine) bonds.[3,4] The chelating N(1)–Mn–N(2) bond angle of 74.8(2)° is, as anticipated, much smaller than the other *cis* angles in the cation, which range from 94.0(2) to 98.3(2)°; the largest *cis* angles are associated with the face occupied by the pyridine moieties, i.e. the N(1)–Mn–N(1′) angles. The *trans* N(1)–Mn–N(2) angles are 166.6(2)°. This observed chelating angle of 74.8(2)° is smaller than the average values of 75.8(3)–81.6(2)° in the *mer* isomers or those of 79.7(2)–83.38(7)° in the iron(II) *fac* isomers.

The ligand pyridine ring and the exocyclic atom C(7) are roughly coplanar, the maximum deviation from the least-squares plane being 0.018 Å while the average deviation is 0.010 Å. Ligand atom N(2) lies 0.625 Å below this plane, on the same side of the plane as manganese. The five-membered ring formed by Mn, N(1), C(2), C(7) and N(2) is in the envelope conformation, the four atoms Mn, N(1), C(2) and N(2) being approximately coplanar (with a maximum deviation from the least-squares plane of 0.009 Å) while atom C(7) lies 0.40 Å above this plane. The consequent N(1)–C(2)–C(7)–N(2) torsion angle is 31.9°.

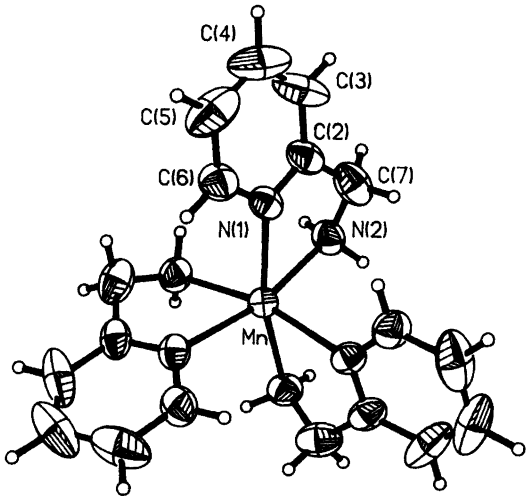

Fig. 1. View of the *fac*-$[Mn(pico)_3]^{2+}$ cation in the crystals of the perchlorate salt. Unlabelled C and N atoms are related to the labelled ones by the C_3 axis passing through Mn.

The amine nitrogen atom N(2) participates in two hydrogen bonds to the perchlorate ion centered on Cl(1). Atom Cl(1) sits on the three-fold axis, and a given amine nitrogen atom donates a hydrogen bond to two different oxygen atoms connected to two different Cl(1) centers. The N···O and H···O distances and associated N–H···O angles are 3.185(9), 2.26 Å and 163° and 3.319(10), 2.59 Å and 113°, respectively.

Table 3. Bond lengths (Å) in the $[Mn(pico)_3]^{2+}$ cation.

Atoms	Distance	Atoms	Distance
Mn–N(1)	2.266(5)	Mn–N(2)	2.266(6)
N(1)–C(2)	1.338(8)	N(1)–C(6)	1.339(9)
C(2)–C(3)	1.352(11)	C(2)–C(7)	1.501(11)
C(3)–C(4)	1.355(17)	C(4)–C(5)	1.364(15)
C(5)–C(6)	1.374(12)	C(7)–N(2)	1.437(10)

Table 4. Bond angles (°) in the $[Mn(pico)_3]^{2+}$ cation.

Atoms[a]	Angle	Atoms[a]	Angle
N(1)–Mn–N(2)	74.8(2)	N(1)–Mn–N(1A)	98.3(2)
N(1)–Mn–N(2A)	94.0(2)	N(2)–Mn–N(1A)	166.6(2)
N(2)–Mn–N(2A)	94.1(2)	Mn–N(1)–C(2)	115.4(4)
Mn–N(1)–C(6)	124.0(4)	C(2)–N(1)–C(6)	119.0(6)
N(1)–C(2)–C(3)	121.0(7)	N(1)–C(2)–C(7)	116.7(6)
C(3)–C(2)–C(7)	112.3(7)	C(2)–C(3)–C(4)	120.7(9)
C(3)–C(4)–C(5)	118.9(9)	C(4)–C(5)–C(6)	119.0(9)
N(1)–C(6)–C(5)	121.4(7)	C(2)–C(7)–N(2)	112.8(6)
Mn–N(2)–C(7)	111.5(4)		

[a] Atoms N(1A) and N(2A) are related to N(1) and N(2), respectively, by the symmetry operation *z,x,y*.

* Hydrogen atom coordinates, anisotropic displacement parameters and observed and calculated structure amplitudes are available from the authors (D.J.H.) as supplementary material.

There are 16 perchlorate anions in the cell, centered on three independent chlorine atoms Cl(1), Cl(2) and Cl(3). Atom Cl(1) lies on the three-fold axis, and accounts for eight of the 16 chlorine atoms in the cell. The oxygen atoms associated with this chlorine atom are O(11) (which also lies on the three-fold axis) and O(12), which is in a general position. The other perchlorate anions, which do not participate in hydrogen bonding, are extensively disordered, but (presumably as a result of the hydrogen bonding) the perchlorate centered on Cl(1) is ordered with Cl–O distances ranging from 1.387(4) to 1.404(7) Å and O–Cl–O angles of 109.3(3) to 109.6(3)°. Chlorine atom Cl(2) lies on a position of 23 (T) symmetry, and accounts for two of the 16 chlorine atoms in the cell. There are two independent sets of tetrahedral oxygen positions associated with this chlorine atom, represented by atoms O(21) and O(22); each of these positions is equally occupied, leading to a 50/50 disorder at this site. Atom Cl(3) lies on a position of 222 (D_2) symmetry, and accounts for the remaining six chlorine atoms in the cell. Examination of a difference Fourier map suggests that the 24 oxygen atoms associated with this center are disordered among three positions, O(31), O(32) and O(33). An analysis of the thermal parameters of these oxygen atoms suggests that O(32) has an occupancy of 50 % (12 oxygen atoms), O(31) has an occupancy of 25 % (six atoms), and O(33) (which sits on the two-fold axis parallel to a) has an occupancy of 25 % (six atoms). While this model accounts for all peaks in the difference Fourier map and leads to an acceptable description of the thermal motion of all atoms involved, the resultant geometrical parameters indicate that it is clearly only approximately correct. Thus, the Cl(3)–O bond lengths are in the broad range of 1.25(2) to 1.50(2) Å, and angles in the presumed tetrahedral moieties range from 80 to 130°. Obviously, therefore, while these positions are able to account for the residual electron density they can only be regarded as a crude model for what is probably much more extensive disorder at this site.

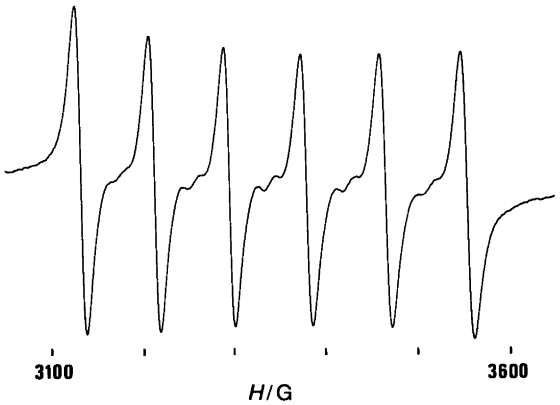

Fig. 2. The EPR spectrum (X-band) of a 0.5 % solution of *fac*-[Mn(pico)$_3$](ClO$_4$)$_2$ dissolved in the isomorphous zinc host complex.

The magnetic susceptibility was measured in the range 4–300 K. The calculated effective magnetic moment was constant from 20 to 300 K ($\mu_{eff} = 5.92$). This indicates that the complex is high-spin Mn(II), $S = 5/2$.

The EPR spectrum of the manganese complex as a 0.5 % solution in the isomorphous zinc host is shown in Fig. 2. The spectrum is a classical example of the expected six-line pattern for an octahedral manganese(II) ($I = 5/2$, $S = 5/2$) complex. Relevant parameters have been calculated from the field positions of the second-derivative spectrum using a second-order perturbation treatment described elsewhere.[11] The calculated values of the parameters are $g = 2.00$, $|A| = 79.0 \times 10^{-4}$ cm^{-1}. With a frequency of 9.39 GHz and $S = 5/2$, $I = 5/2$, the maximum deviation between observed and calculated field positions was 0.4 G. The observed linewidth of 24 G is reasonable, since all six ligating atoms have $I = 1$. Superhyperfine splittings could not be observed at low modulation amplitude.

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