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Synthesis and Characterization of Bis(2-pyridylmethyl)amine Complexes of Manganese(II), Zinc(II), and Cadmium(II)

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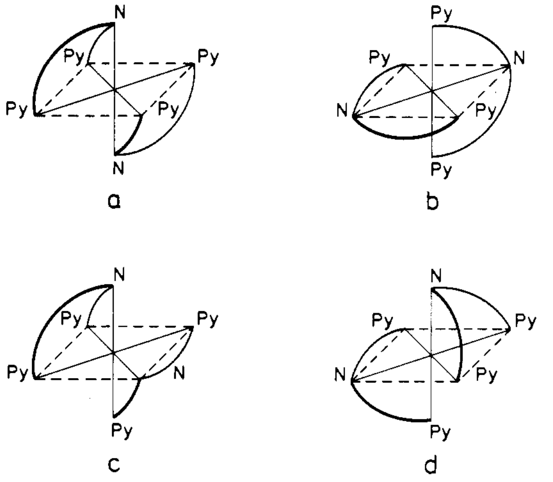
Complexes of the general formulation $[M(bispicam)_2]X_2$ [where bispicam is bis(2-pyridylmethyl)amine, $C_{12}H_{13}N_3$, and M is Mn(II), Zn(II), or Cd(II)] have been synthesized and characterized by X-ray crystallography and by EPR and ^{13}C NMR spectroscopy. All of the complexes are facial isomers, but three distinct structural types have been discovered. The manganese complex $[Mn(bispicam)_2](ClO_4)_2$ (**1**) crystallizes in the space group $C2/c$ of the monoclinic system with four molecules in a cell of dimensions $a = 20.594$ (4) Å, $b = 11.011$ (2) Å, $c = 13.715$ (3) Å, and $\beta = 114.845$ (15)°. The manganese atom in **1** sits on a crystallographic 2-fold axis. The cadmium complex $[Cd(bispicam)_2](ClO_4)_2$ (**2**) is isomorphous with **1**, with cell dimensions $a = 20.670$ (4) Å, $b = 10.911$ (3) Å, $c = 13.953$ (2) Å, and $\beta = 114.493$ (13)°. The zinc complex $[Zn(bispicam)_2](ClO_4)_2$ (**3**) also crystallizes in the space group $C2/c$ of the monoclinic system but with eight molecules in a cell of dimensions $a = 23.715$ (6) Å, $b = 9.006$ (2) Å, $c = 26.052$ (11) Å, and $\beta = 91.52$ (3)°. There are two crystallographically independent cations in the crystals of **3**, in one of which the zinc atom sits on a crystallographic 2-fold axis as in **1** and **2** and in the other of which zinc sits on a crystallographic inversion center. The chloride salt of the zinc complex, $[Zn(bispicam)_2]Cl_2{\cdot}6H_2O$ (**4**), crystallizes in the space group $P2_1/c$ of the monoclinic system with two molecules in a cell of dimensions $a = 9.175$ (2) Å, $b = 10.088$ (2) Å, $c = 16.472$ (3) Å, and $\beta = 94.540$ (10)°. The zinc atom in **4** sits on a crystallographic inversion center, so the isomer found here is similar to one of those in **3**. The EPR spectrum of Mn doped in the crystals of **2** reveals the presence of the anticipated geometry at Mn, and this spectrum has been very successfully simulated by diagonalization of the energy matrix. The EPR spectrum of Mn doped in the crystals of **3** demonstrates that, at low concentrations, the manganese atoms evidently occupy only the sites of C_2 symmetry, the resulting spectrum being very similar to that of Mn doped in **2**; this spectrum has also been precisely simulated. The ^{13}C NMR spectra of the complexes demonstrate that NMR techniques will be of value in distinguishing between the various isomers in this and other diamagnetic zinc and cadmium series.

Introduction

Measuring EPR spectra of crystalline solids generally requires that the compounds can be diluted in a diamagnetic host. And even if it is possible to prepare a similar diamagnetic compound, several problems are often encountered because of different structures, different sizes, and different sites in the host lattice. We will here discuss such problems with the 1:2 manganese(II) complexes with the ligand bis(2-pyridylmethyl)amine, $C_{12}H_{13}N_3$ (bispicam), diluted in the similar zinc(II) and cadmium(II) complexes.

Bispicam is an example of a tridentate ligand where the two terminal coordination sites are identical to each other but different from the central site. For a system of this type, the three potential geometric isomers a–d are shown in the following diagrams. Of these, one isomer (b) is the meridional isomer while the others are facial, and c and d are enantiomers. For the mer isomer (b) there are actually three isomeric forms because of the relative positions of the hydrogen atoms on the amine nitrogen atoms.[2]



In the present series, we have isolated both of the *fac* isomers but have not observed the *mer* isomer (b). *Mer* coordination has, however, been seen in the structure of the smaller chromium(III) ion, where we have earlier reported the structure of a binuclear complex containing this ligand.[3] The related species $[M(pico)_3]^{2+}$ [where pico is the bidentate ligand (2-pyridylmethyl)amine, which contains only one of the two identical "arms" of bispicam] have been shown to exist as *fac* isomers in the solid state.[4] The EPR spectrum of this compound contains the usual six hyperfine lines, which means that the zero-field splitting (zfs) is very small. In fact, the spectrum has been interpreted with a zfs equal to zero.

For compounds with a considerable zfs, the interpretation of the spectra has often been based on plots of the transitions as function of D (zfs parameter) and B (field strength).[5] With this kind of interpretation, it is crucial that the lines at the highest

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Table I. Crystallographic and Data Collection Parameters

	1	2	3	4
formula	$C_{24}H_{26}Cl_2MnN_6O_8$	$C_{24}H_{26}N_6O_8Cl_2Cd$	$C_{24}H_{26}N_6O_8Cl_2Zn$	$C_{24}H_{38}Cl_2N_6O_6Zn$
system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$
a (Å)	20.594 (4)	20.670 (4)	23.715 (6)	9.175 (2)
b (Å)	11.011 (2)	10.911 (3)	9.006 (2)	10.088 (2)
c (Å)	13.715 (3)	13.953 (2)	26.052 (11)	16.472 (3)
β (deg)	114.845 (15)	114.493 (13)	91.52 (3)	94.540 (10)
V (Å^3)	2822.2 (10)	2863.6 (10)	5562 (3)	1519.8 (5)
Z	4	4	8	2
T (°C)	23	23	22	22
μ (mm^{-1})	0.695	1.002	1.153	1.048
index ranges	$0 \leq h \leq 26$	$0 \leq h \leq 29$	$0 \leq h \leq 28$	$-9 \leq h \leq 0$
	$0 \leq k \leq 14$	$0 \leq k \leq 15$	$0 \leq k \leq 10$	$0 \leq k \leq 10$
	$-17 \leq l \leq 17$	$-19 \leq l \leq 19$	$-30 \leq l \leq 30$	$-17 \leq l \leq 17$
2θ range (deg)	$4.0 \leq 2\theta \leq 55$	$4.0 \leq 2\theta \leq 60$	$4.0 \leq 2\theta \leq 50$	$4.0 \leq 2\theta \leq 45$
no. of reflns	3519	4506	5412	2292
no. of obsd reflns	2384	3153	2348	1244
R	0.0449	0.0489	0.0423	0.0385
R_w	0.0673	0.0714	0.0406	0.0561

field strength are correctly identified, because the line which is from the z orientation at the highest field strength is often so weak that it can hardly be observed. For the interpretation of the spectra in this work, we have used a simulation program where the energy matrices have been solved by diagonalization rather than by perturbation methods. To our knowledge, this represents the first successful simulation of such a complicated system.

Experimental Section

Syntheses. Bis(2-pyridylmethyl)amine trihydrochloride hydrate was prepared as described elsewhere.[6]

(i) $[Mn(C_{12}H_{13}N_3)_2](ClO_4)_2$ (1). Bispicam·3HCl·H$_2$O (0.49 g, 1.5 mmol) was dissolved in water (2.5 mL). A solution of sodium hydroxide (2 mL, 2 M) was added, followed by a solution of manganese(II) chloride tetrahydrate (0.148 g, 0.75 mmol). Nitrogen was bubbled through the solution, and the pH of the solution was adjusted to 8 by means of a solution of sodium hydroxide. After 30 min, the solution was filtered, and a solution of lithium perchlorate was added to the filtrate. White crystals separated. They were filtered off and washed with ethanol (96%). Yield: 0.39 g (80%). Anal. Calcd for $[Mn(C_{12}H_{13}N_3)_2](ClO_4)_2$: Mn, 8.42; C, 44.19; N, 12.88; H, 4.02; Cl, 10.87. Found: Mn, 8.41; C, 44.15; N, 12.81; H, 3.95; Cl, 10.96. The compound was recrystallized from boiling water. The subsequent single-crystal X-ray analysis revealed that this is the C_2 isomer (c and d).

(ii) $[Cd(C_{12}H_{13}N_3)_2](ClO_4)_2$ (2). This complex was synthesized as described above but from cadmium chloride hydrate (0.15 g, 0.75 mmol). Nitrogen was omitted. Yield: 0.27 g (50%). Anal. Calcd for $[Cd(C_{12}H_{13}N_3)_2](ClO_4)_2$: C, 40.61; N, 11.84; H, 3.69; Cl, 9.99. Found: C, 40.45; N, 11.87; H, 3.66; Cl, 9.66. The compound was recrystallized from boiling water. X-ray powder diagrams revealed that the crystals are isomorphous with **1** and contain the C_2 isomer.

(iii) $[Zn(C_{12}H_{13}N_3)_2](ClO_4)_2$ (3). This complex was synthesized as described above but from zinc nitrate hexahydrate (0.223 g, 0.75 mmol). Yield: 0.45 g (91%). Anal. Calcd for $[Zn(C_{12}H_{13}N_3)_2](ClO_4)_2$: C, 43.49; N, 12.68; H, 3.95; Cl, 10.70. Found: C, 43.56; N, 12.74; H, 3.98; Cl, 10.75. X-ray powder diagrams showed two kinds of crystals, but when the compound was recrystallized from boiling water only one form was found; the subsequent single-crystal X-ray analysis revealed that this is a crystal containing both the C_2 isomer (c and d) and the C_i isomer (a). In one case, crystals isomorphous with **1** were obtained, but in that case, a crystal of the manganese complex was used to initiate crystallization. For purposes of reference, we call this sample **3a**.

(iv) $[Zn(C_{12}H_{13}N_3)_2](ClO_4)_2$. When ethanol replaced water as a solvent, powdery crystals of a new type were always obtained. Regrettably, we were unable to obtain crystals suitable for X-ray structural analysis, but it seems probable that this is the pure C_i isomer (a) (vide infra).

(v) $[Zn(C_{12}H_{13}N_3)_2]Cl_2·6H_2O$ (4). These crystals were obtained when a solution of the amine as described above was allowed to react with a solution of zinc chloride (0.102 g, 0.75 mmol) at a pH of 9. After the solution was allowed to stand for some days, large crystals separated. They were filtered off and washed with ethanol (96%). Yield: 0.20 g (42%). Anal. Calcd for $[Zn(C_{12}H_{13}N_3)_2]Cl_2·6H_2O$: C, 44.85; N, 13.08; H, 6.09; Cl, 11.03. Found: C, 44.97; N, 13.23; H, 5.57; Cl, 11.28. The subsequent single-crystal X-ray analysis revealed that this form is the C_i isomer (a). When the compound was dissolved in *cold* water and a solution of sodium perchlorate was added, perchlorate salt crystals of type iv (above) separated, which lends credence to our suggestion that this is the perchlorate salt of the C_i isomer (a).

(vi) $[Mn/Cd(C_{12}H_{13}N_3)_2](ClO_4)_2$. The crystals were obtained as described above but using a mixture of manganese(II) chloride tetrahydrate (0.030 g, 0.15 mmol) and cadmium chloride hydrate (0.54 g, 27 mmol). The resulting product was recrystallized from water and contained approximately 4% manganese based on the total content of metal; the crystals are isomorphous with **1**.

(vii) $[Mn/Zn(C_{12}H_{13}N_3)_2](ClO_4)_2$. The crystals were obtained as described above but using a mixture of manganese(II) chloride tetrahydrate (0.015 g, 0.075 mmol) and zinc nitrate hexahydrate (0.42 g, 1.4 mmol). The resulting product was recrystallized from water and contained approximately 3% manganese based on the total content of metal; the crystals are isomorphous with **3**.

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

Physical Measurements. EPR spectra were recorded at several temperatures down to 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 5 G, and microwave power of 10 mW. Samples were examined as solid solutions. NMR spectra were recorded at room temperature on a Bruker MSL 300 spectrometer. Samples were examined as solids.

X-ray Data Collection and Reduction. The structures of the complexes $[Mn(bispicam)_2](ClO_4)_2$ (**1**), $[Cd(bispicam)_2](ClO_4)_2$ (**2**), $[Zn(bispicam)_2](ClO_4)_2$ (**3**), and $[Zn(bispicam)_2]Cl_2·6H_2O$ (**4**) were determined at room temperature (295–296 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda(K\alpha_1)$ = 0.709 26 Å, $\lambda(K\alpha_2)$ = 0.713 54 Å) and a graphite monochromator. Crystal data and experimental parameters are collected in Table I. The structures were all solved by direct methods and refined by full-matrix least-squares procedures. Hydrogen atom parameters were allowed to vary only in the refinement of **3**, those in all other structures being constrained to reasonable geometry (C–H = 0.96 Å). All programs (including atomic scattering factors and dispersion corrections) were from the SHELXTL-PLUS system.[7]

$[Mn(bispicam)_2](ClO_4)_2$ (1). The complex crystallizes as colorless plates in the monoclinic space group $C2/c$, with four molecules in the unit cell. Hence, there is only one crystallographically independent cation in the cell, and it is constrained to exhibit either C_2 or C_i symmetry at manganese. The final values of the agreement factors R and R_w were 0.0449 and 0.0673, respectively, based on 2384 observed independent

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

	x	y	z	U(eq)[a]
Mn	0	1571 (1)	7500	36 (1)
N(1A)	839 (1)	125 (2)	8028 (2)	47 (1)
N(1B)	−336 (1)	2133 (2)	8832 (2)	46 (1)
N(2)	960 (1)	2476 (2)	8787 (2)	47 (1)
C(2A)	829 (2)	−848 (3)	7435 (3)	57 (1)
C(3A)	1419 (2)	−1547 (3)	7611 (3)	68 (2)
C(4A)	2057 (2)	−1191 (4)	8434 (4)	75 (2)
C(5A)	2080 (2)	−206 (4)	9046 (3)	67 (1)
C(6A)	1456 (1)	443 (3)	8828 (2)	49 (1)
C(7A)	1417 (2)	1516 (3)	9478 (2)	61 (1)
C(2B)	−925 (2)	1770 (3)	8939 (3)	52 (1)
C(3B)	−1095 (2)	2163 (3)	9753 (3)	56 (1)
C(4B)	−646 (2)	2971 (3)	10490 (3)	60 (1)
C(5B)	−38 (2)	3361 (3)	10394 (3)	55 (1)
C(6B)	100 (2)	2924 (2)	9555 (2)	46 (1)
C(7B)	739 (2)	3365 (3)	9387 (3)	63 (1)
Cl	3216 (1)	51 (1)	2222 (1)	59 (1)
O(1)	2995 (2)	1261 (3)	1909 (3)	81 (1)
O(2)	3454 (4)	−16 (9)	3345 (5)	85 (3)
O(3)	3634 (7)	−321 (7)	1763 (10)	117 (6)
O(4)	2553 (4)	−623 (6)	1777 (6)	110 (3)
O(5)	3003 (12)	−888 (11)	1447 (10)	131 (9)
O(6)	3223 (17)	−588 (19)	3052 (19)	131 (13)
O(7)	4042 (8)	11 (15)	2372 (14)	94 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **2**

	x	y	z	U(eq)[a]
Cd	5000	1653 (1)	2500	36 (1)
N(1A)	5336 (2)	2206 (3)	1127 (3)	44 (1)
N(1B)	4128 (2)	120 (3)	1950 (3)	47 (1)
N(2)	4011 (2)	2505 (3)	1128 (3)	47 (1)
C(2A)	5933 (3)	1850 (4)	1045 (4)	52 (2)
C(3A)	6089 (3)	2214 (5)	210 (4)	58 (2)
C(4A)	5630 (3)	2966 (5)	−542 (4)	59 (2)
C(5A)	5016 (3)	3345 (4)	−464 (4)	58 (2)
C(6A)	4886 (3)	2938 (4)	391 (3)	47 (2)
C(7A)	4234 (3)	3370 (5)	521 (5)	64 (2)
C(2B)	4130 (3)	−841 (5)	2548 (5)	62 (2)
C(3B)	3527 (4)	−1511 (5)	2355 (6)	72 (3)
C(4B)	2923 (3)	−1204 (7)	1559 (6)	81 (3)
C(5B)	2900 (2)	−192 (6)	935 (4)	70 (2)
C(6B)	3532 (2)	443 (5)	1142 (3)	48 (1)
C(7B)	3587 (3)	1486 (5)	477 (3)	60 (2)
Cl	1795 (1)	−67 (1)	2807 (1)	61 (1)
O(1)	2004 (2)	−1287 (4)	3106 (4)	74 (2)
O(2)	1574 (3)	112 (7)	1739 (4)	123 (3)
O(3)	2414 (5)	640 (7)	3310 (6)	172 (5)
O(4)	1295 (5)	279 (7)	3143 (7)	216 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

intensities with $F > 6.0\sigma(F)$. The final values of the atomic coordinates are presented in Table II.

[Cd(bispicam)$_2$](ClO$_4$)$_2$ (2). The crystals are isomorphous with those of **1**. The final values of the agreement factors R and R_w were 0.0489 and 0.0714, respectively, based on 3153 observed independent intensities with $F > 6.0\sigma(F)$. The final values of the atomic coordinates are presented in Table III.

[Zn(bispicam)$_2$](ClO$_4$)$_2$ (3). The complex crystallizes in the monoclinic space group $C2/c$, with eight molecules in the unit cell. With eight molecules in space group $C2/c$, no constraint is imposed on the geometry of the cation. In fact, however, the structure solution revealed that there are two crystallographically independent cations in the cell, each of which is therefore constrained as above for **1**. The final values of the agreement factors R and R_w were 0.0423 and 0.0406, respectively, based on 2348 observed independent intensities with $F > 6.0\sigma(F)$. The final values of the atomic coordinates are presented in Table IV.

[Zn(bispicam)$_2$]Cl$_2$·6H$_2$O (4). The complex crystallizes in the monoclinic space group $P2_1/c$, with two molecules in the unit cell. Hence, there is only one crystallographically independent cation in the cell, and it is constrained to exhibit C_i (inversion) symmetry at zinc. The final values of the agreement factors R and R_w were 0.0449 and 0.0673, respectively, based on 2384 observed independent intensities with $F > 6.0\sigma(F)$. The final values of the atomic coordinates are presented in Table V.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **3**

	x	y	z	U(eq)[a]
Zn(1)	0	−83 (1)	2500	38 (1)
N(1A)	−134 (2)	1664 (6)	3056 (2)	40 (2)
C(2A)	76 (3)	1425 (8)	3527 (3)	41 (2)
C(3A)	−33 (4)	2421 (12)	3931 (3)	63 (3)
C(4A)	−351 (4)	3644 (12)	3824 (4)	75 (4)
C(5A)	−560 (3)	3893 (10)	3340 (4)	63 (3)
C(6A)	−440 (3)	2874 (9)	2969 (3)	54 (3)
C(7A)	428 (3)	71 (9)	3602 (3)	51 (3)
N(1B)	829 (2)	−990 (6)	2462 (2)	40 (2)
C(2B)	1008 (3)	−1967 (7)	2821 (2)	41 (2)
C(3B)	1534 (3)	−2594 (9)	2810 (3)	53 (3)
C(4B)	1886 (3)	−2237 (8)	2412 (3)	52 (3)
C(5B)	1700 (3)	−1273 (9)	2041 (3)	52 (3)
C(6B)	1176 (3)	−669 (8)	2087 (3)	47 (3)
C(7B)	598 (3)	−2374 (10)	3229 (3)	59 (3)
N(2)	196 (3)	−1157 (7)	3290 (2)	48 (2)
Zn(2)	7500	2500	5000	34 (1)
N(21A)	7330 (2)	1922 (6)	5785 (2)	37 (2)
C(22A)	7356 (2)	467 (7)	5878 (2)	38 (2)
C(23A)	7218 (3)	−129 (9)	6348 (3)	56 (3)
C(24A)	7051 (3)	798 (10)	6729 (3)	59 (3)
C(25A)	7016 (3)	2284 (9)	6639 (3)	48 (3)
C(26A)	7157 (3)	2810 (8)	6166 (3)	47 (3)
C(27A)	7568 (4)	−513 (8)	5460 (3)	48 (3)
N(21B)	6617 (2)	2140 (5)	4835 (2)	37 (2)
C(22B)	6481 (3)	750 (7)	4721 (2)	37 (2)
C(23B)	5934 (3)	317 (9)	4616 (3)	56 (3)
C(24B)	5511 (3)	1365 (11)	4659 (3)	59 (3)
C(25B)	5646 (3)	2775 (11)	4792 (3)	53 (3)
C(26B)	6200 (3)	3148 (9)	4875 (3)	47 (3)
C(27B)	6957 (3)	−347 (8)	4678 (3)	51 (3)
N(22)	7486 (2)	110 (6)	4942 (2)	35 (2)
Cl(1)	3447 (1)	1847 (2)	6701 (1)	52 (1)
O(1)	2965 (2)	929 (7)	6647 (2)	93 (3)
O(2)	3392 (3)	2859 (8)	7114 (2)	114 (3)
O(3)	3939 (2)	970 (6)	6782 (2)	98 (3)
O(4)	3512 (2)	2648 (7)	6238 (2)	94 (3)
Cl(2)	1034 (1)	1781 (2)	5617 (1)	51 (1)
O(5)	1603 (2)	1391 (6)	5684 (2)	85 (2)
O(6)	885 (3)	1792 (7)	5090 (2)	106 (3)
O(7)	937 (3)	3105 (9)	5849 (3)	181 (5)
O(8)	711 (3)	694 (10)	5844 (3)	148 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Hydrogen atom parameters and anisotropic thermal parameters for all four structures are available as supplementary material.

Results and Discussion

Description of the Structures. The manganese atom in **1** lies on a site of C_2 symmetry, the 2-fold axis relating one ligand to the other. A view of the cation is shown in Figure 1, and the principal bond lengths and angles are listed in Table VI.

The geometry at the manganese atom is pseudooctahedral, as anticipated, and the isomer isolated here is the *fac* isomer represented by c and d above; the isomer shown in Figure 1 corresponds to d, but in this centrosymmetric space group, there is an equal distribution of the two enantiomers, of course. The Mn–N(amine) bond of length 2.255 (2) Å is intermediate in length between the two Mn–N(py) bonds of 2.235 (2) and 2.294 (3) Å; in *fac*-[Mn(pico)$_3$]$^{2+}$, the Mn–N bonds are also indistinguishable,[4] but in *fac*-[Fe(pico)$_3$]$^{2+}$, the Fe–N(py) bonds are significantly shorter than the Fe–N(amine) bonds.[8] In *mer*-[(C$_4$O$_4$)(bispicam)Cr(OH)]$_2$, the (axial) Cr–N(py) bonds are longer than the Cr–N(amine) bond.[3] The N(py)–Mn–N(amine)

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Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **4**

	x	*y*	*z*	*U*(eq)[a]
Zn(1)	0	0	0	37 (1)
N(1A)	−567 (4)	1890 (4)	−561 (3)	39 (2)
N(1B)	−279 (4)	1053 (5)	1152 (3)	41 (2)
N(2)	−2344 (4)	−65 (4)	11 (3)	39 (1)
C(2A)	319 (7)	2920 (6)	−670 (3)	45 (2)
C(3A)	−167 (7)	4146 (6)	−921 (4)	55 (2)
C(4A)	−1643 (8)	4323 (7)	−1044 (4)	62 (3)
C(5A)	−2572 (7)	3297 (6)	−927 (4)	51 (2)
C(6A)	−2013 (6)	2082 (5)	−690 (3)	39 (2)
C(7A)	−2960 (6)	880 (6)	−590 (4)	45 (2)
C(2B)	684 (6)	1828 (6)	1566 (4)	47 (2)
C(3B)	303 (7)	2762 (7)	2110 (4)	56 (2)
C(4B)	−1136 (8)	2895 (7)	2247 (4)	59 (3)
C(5B)	−2162 (7)	2091 (7)	1830 (4)	55 (2)
C(6B)	−1694 (6)	1160 (6)	1297 (3)	43 (2)
C(7B)	−2732 (6)	207 (6)	845 (3)	50 (2)
Cl(1)	4118 (2)	2752 (2)	486 (1)	62 (1)
O(1W)	5882 (6)	−1528 (6)	2642 (3)	90 (2)
O(2W)	3956 (6)	617 (6)	2566 (3)	92 (2)
O(3W)	3434 (6)	20 (5)	4156 (3)	83 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

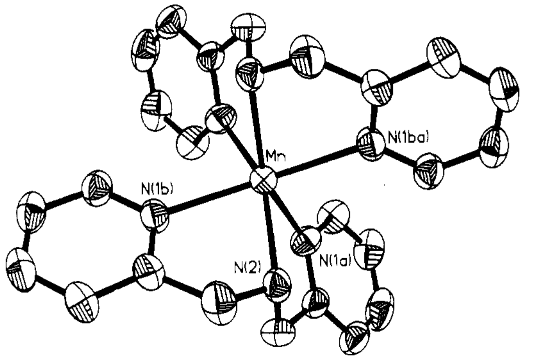

Figure 1. View of the $[Mn(bispicam)_2]^{2+}$ cation in the crystals of **1**. Hydrogen atoms are omitted for clarity. Unlabeled atoms are related to labeled atoms by the C_2 axis, which is coming out of the page toward the reader. The structures of the cadmium analogue $[Cd(bispicam)_2]^{2+}$ in **2** and of the $[Zn(bispicam)_2]^{2+}$ cation in the crystals of **3** centered on atom Zn(1) (and having C_2 symmetry at zinc) are substantially similar to this structure.

bond angles are 73.5 (1) and 75.9 (1)°, while the N(py)–Mn–N(py) angle is 112.6 (1)°.

The structure of the cadmium complex **2** is very similar to that of **1**, the two crystals being isomorphous. The principal bond lengths and angles of **2** are compared with those of **1** in Table VI. The Cd–N bonds of 2.338 (3)–2.370 (4) Å are slightly longer than the Mn–N bonds in **1**, but the structural differences between the two cations are minimal. The perchlorate anions in the crystals of **2** are apparently ordered, the Cl–O bonds of 1.354 (13)–1.408 (4) Å and associated O–Cl–O angles of 105.5 (4)–112.2 (4)° being normal. In the manganese complex **1**, the perchlorate ions are disordered in two sets of positions around a pseudo-3-fold axis along Cl–O(1); this kind of perchlorate disorder has been observed in several other structures.[9,10]

Table VI. Selected Bond Lengths (Å) and Angles (deg) for the C_2 Isomers in **1**–**3**[a]

	1 (M = Mn)	**2** (M = Cd)	**3** (M = Zn)
	Lengths		
M–N(1A)	2.235 (2)	2.343 (4)	2.168 (5)
M–N(1B)	2.294 (3)	2.370 (4)	2.133 (5)
M–N(2)	2.255 (2)	2.338 (3)	2.311 (6)
	Angles		
N(1A)–M–N(1B)	112.6 (1)	111.1 (1)	117.4 (2)
N(1A)–M–N(2)	75.9 (1)	73.9 (1)	74.8 (2)
N(1A)–M–N(1A′)	89.2 (1)	88.8 (2)	86.9 (3)
N(1A)–M–N(1B′)	90.0 (1)	90.2 (1)	95.4 (2)
N(1A)–M–N(2′)	150.8 (1)	147.7 (1)	150.4 (2)
N(1B)–M–N(2)	73.5 (1)	71.7 (1)	73.6 (2)
N(1B)–M–N(1B′)	148.7 (1)	150.5 (2)	130.5 (3)
N(1B)–M–N(2′)	92.6 (1)	96.4 (1)	87.8 (2)
N(2)–M–N(2′)	127.5 (1)	133.1 (2)	130.5 (3)

[a] For consistency, the atomic numbering scheme used in this table corresponds to that used for **1** and **3** in Tables II and IV, but not to that used for **2** in Table III. For complex **2**, N(1B) in this table corresponds to atom N(1A) in Table III, and vice versa.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for the C_i Isomers in **3** and **4**

	3	**4**
	Lengths	
Zn–N(1A)	2.160 (5)	2.164 (4)
Zn–N(1B)	2.150 (5)	2.207 (5)
Zn–N(2)	2.158 (5)	2.154 (4)
	Angles	
N(1A)–Zn–N(1B)	87.0 (2)	84.4 (2)
N(1A)–Zn–N(2)	79.8 (2)	79.8 (2)
N(1A)–Zn–N(1B′)	93.0 (2)	95.6 (2)
N(1A)–Zn–N(2′)	100.2 (2)	100.2 (2)
N(1B)–Zn–N(2)	79.8 (2)	79.8 (2)
N(1B)–Zn–N(2′)	100.2 (2)	100.2 (2)

There are two crystallographically independent zinc ions in the crystals of **3**, each lying on a special position. Atom Zn(1) lies on a site of C_2 symmetry, the resulting cation resembling those in **1** and **2**. The principal bond lengths and angles are compared with those of **1** and **2** in Table VI. In this complex, which is isoelectronic with **2**, the Zn–N(amine) bond is evidently longer than the Zn–N(py) bond, but no electronic significance can be attached to this observation in view of their similarity in **2**.

Atom Zn(2), however, lies on a crystallographic inversion center and exhibits C_i symmetry. This isomer corresponds to isomer a above; the principal bond lengths and angles are listed in Table VII. In this isomer, the three independent Zn–N bond lengths are all similar and lie in the narrow range 2.150 (5)–2.160 (5) Å. In this C_i isomer, the bond angles subtended by the ligand at the metal are less strained than those in the C_2 isomers; thus, the N(amine)–Zn(2)–N(py) angles here are 79.8 (2)°, while at Zn(1) they are 73.6 (2) and 74.8 (2)°.

The perchlorate anions in **3** are both ordered and well behaved, with Cl–O bond lengths in the range 1.359 (8)–1.421 (6) Å and O–Cl–O angles of 107.0 (4)–111.2 (4)°.

The zinc atom in **4** lies on an inversion center, giving rise to the C_i isomer a seen at the Zn(2) site of **3**. A view of this cation is shown in Figure 2, and the principal bond lengths and angles are compared with those at Zn(2) in **3** in Table VII. An examination of this table demonstrates that the two examples of this isomer are extremely similar in structure.

NMR Spectra. The ^{13}C NMR spectra of the diamagnetic complexes **3a**(C_2), **3**(C_2 and C_i) and **4**(C_i) are shown in Figure 3. As can be readily seen from inspection of this figure, NMR spectroscopy can potentially be used to distinguish among these various isomers for the diamagnetic host materials. The two isomers a(C_i) and c(C_2) (or its enantiomer, d) both give relatively simple spectra which are readily distinguished. The aliphatic (low field) region is particularly revealing in this respect. Naturally, the spectrum of **3** is much more complex than either of the others, since it contains sites of both symmetries, but this complexity allows for the identification of this isomorph.

EPR Spectroscopy. The EPR spectrum at 298 K of the manganese(II) complexes doped in the diamagnetic host **2** is

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[9] Hodgson, D. J.; Zietlow, M. H.; Pedersen, E.; Toftlund, H. *Inorg. Chim. Acta* **1988**, *149*, 111–117.

[10] Oki, A. R.; Glerup, J.; Hodgson, D. J. *Inorg. Chem.* **1990**, *29*, 2435–2441.

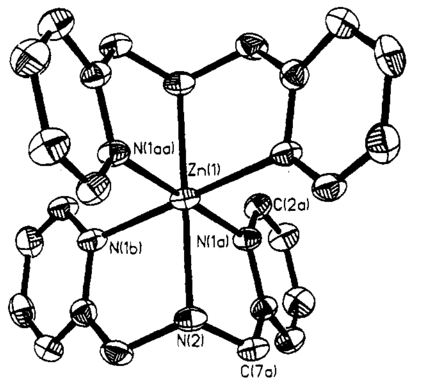

Figure 2. View of the $[Zn(bispicam)_2]^{2+}$ cation in the crystals of **4**. Hydrogen atoms are omitted for clarity. The structure of the $[Zn(bispicam)_2]^{2+}$ cation in the crystals of **3** that is centered on atom Zn(2) and has C_i symmetry at zinc is substantially similar to this structure.

shown in Figure 4 (top). The spectrum has been simulated in order to increase our understanding of manganese(II) EPR spectra. The energy matrix for the $S = {}^5/_2$ state was generated for each orientation of the magnetic field relative to the molecular z axis. The energy matrix was calculated by means of the Hamiltonian

$$\hat{H} = \mu_B H \mathbf{g}\cdot\hat{S} + \hat{S}\cdot\mathbf{A}\cdot\hat{I} + \hat{S}\cdot\mathbf{D'}\cdot\hat{S}$$

with $S = {}^5/_2$ and $I = {}^5/_2$, where all the parameters have their usual meanings. As indicated above in the Hamiltonian expression, it was assumed that the zero-field splitting tensor ($\mathbf{D'}$) and the $\mathbf{A}$ and $\mathbf{g}$ tensors could be diagonalized within the same coordinate framework. All spin Hamiltonian parameters reported here are extracted from the powder spectra and were obtained by a simulation procedure in the manner discussed elsewhere.[11-13] Details of this EPR simulation program will be published in another communication. We note, however, that the spectra are simulated by diagonalization of the full-spin Hamiltonian matrix, which is far more precise than the more traditional (but admittedly quicker) perturbation treatment, since in the latter the nondiagonal terms are neglected; in systems (like the present cases) in which the symmetry at manganese deviates markedly from octahedral, the importance of the nondiagonal terms grows to such an extent that they cannot be neglected.

The resonance condition for each transition was found by successive diagonalizations, and the relative intensities were calculated from the eigenvectors. The total spectrum is then obtained by summation of single-crystal spectra using the formula

$$I(H) = \sum\sum\sum P_i(\beta,\gamma)\, F(H_i - H)\, \Delta\beta\, \Delta\gamma$$

where β and γ are two Euler angles, $N(\beta,\gamma)$ is the number of transitions to be searched, P_i is the transition probability for the ith transition, F is a Lorentzian band shape function, and H_i is the resonant magnetic field for the ith transition. No selection rules were used in our computations. A total number of 540 transitions are thus searched for each orientation of the magnetic field vector with respect to the molecular coordinate system.

Initial values of g_x, g_y, g_z, D, and E were obtained by calculating spectra without considering the nuclear spin. When satisfactory agreement was obtained, the nuclear spin was included and the hyperfine coupling constants were estimated from the spacings between the hyperfine lines. All parameters were then adjusted until a good fit was obtained. Early in the simulation session it became evident that the axial zero-field splitting parameter D and the hyperfine coupling constant A should have the same sign, since the line positions at low magnetic field (0.03–0.12 T) were sensitive to the signs of these parameters. In this and the following simulations we could not observe any deviations from isotropic behavior for the parameters g and A, within the accuracy stated. The simulated spectrum in Figure 4 was obtained using the parameters $g_{iso} = 2.00$, $A_{iso} = -0.0077$ cm^{-1}, $D = -0.1750$ cm^{-1}, and $E = 0$. It is apparent from a comparison of the two curves in Figure 4 that the simulation is virtually perfect.

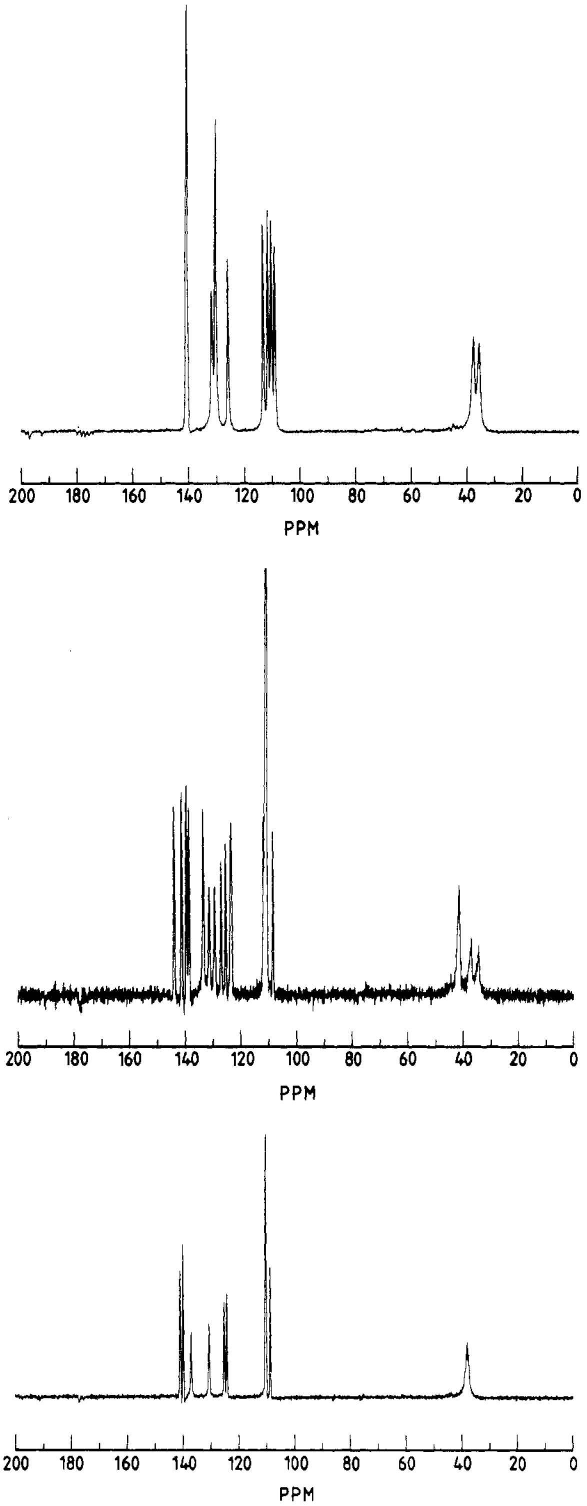

Figure 3. ^{13}C NMR spectra of the diamagnetic species: (a, top) complex **2** (type a); (b, middle) complex **3** (type b); (c, bottom) complex **4** (type c).

The EPR spectrum at 298 K of the manganese(II) complexes doped in the diamagnetic host **3** (Figure 5) is virtually identical to that in Figure 4; the dilution into the smaller zinc lattice,

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(11) Bang, E.; Eriksen, J.; Glerup, J.; Mønsted, L.; Mønsted, O.; Weihe, H. *Acta Chem. Scand.* **1991**, *45*, 367–372.

(12) Glerup, J.; Weihe, H. *Acta Chem. Scand.* **1991**, *45*, 444–448.

(13) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Weihe, H. *Inorg. Chem.* **1991**, *30*, 4909–4914.

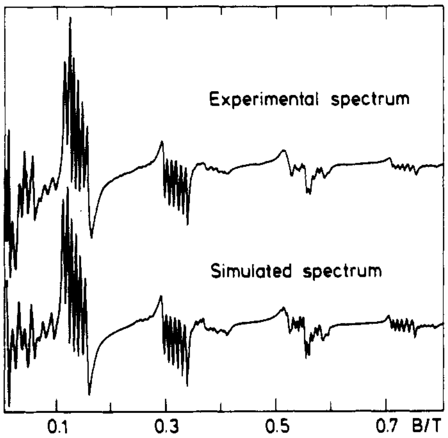

Figure 4. Experimental and simulated EPR spectra of Mn(II) doped into complex **2**. The experimental spectrum was recorded at 298 K. The simulated spectrum was calculated with the following parameters: $g_{iso} = 2.00$, $A_{iso} = -0.0077$ cm^{-1}, $D = -0.1750$, $E = 0$.

however, introduces a minor orthorhombic distortion, while in the larger cadmium lattice the manganese appears to be axial. The spectrum in Figure 5 consists of only one manganese site, as shown by the simulated spectrum, despite the availability in host **3** of two potential sites for manganese. We may deduce from this observation that, at least at the low manganese concentrations (necessarily) used in this procedure, the manganese preferentially replaces zinc atoms of type Zn(1), i.e. the zinc atoms which are lying on sites of C_2 symmetry. This effect may, of course, simply result from the fact that the average Zn(1)–N bond in **3** is slightly longer than the average Zn(2)–N bond, thereby promoting replacement of Zn(1) rather than Zn(2). Using the procedure discussed above, we have simulated this spectrum also, using the parameters $g_{iso} = 2.00$, $A_{iso} = -0.0078$ cm^{-1}, $D = -0.2190$ cm^{-1}, and $E = 0.0058$ cm^{-1}. From the angular dependence of the resonance condition in Figure 5, it is apparent that there is a transition at field strengths above 1 T. We have been unable to observe this transition despite collecting many scans between 1 and 1.5 T. The observed spectrum undergoes some minor changes as a function of temperature, and the spectrum at 70 K is simulated by the parameters $g_{iso} = 2.00$, $A_{iso} = -0.0078$ cm^{-1}, $D = -0.2365$ cm^{-1}, and $E = 0.0034$ cm^{-1}. Agreement between both of these simulated spectra and the observed spectra of Mn doped in **3** are again excellent.

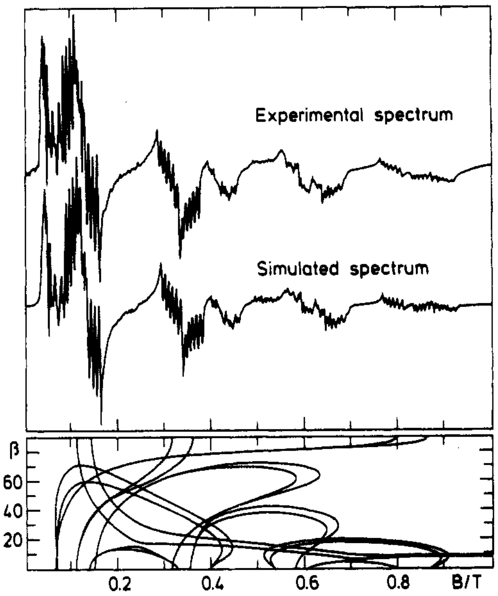

Figure 5. Upper part: Experimental and simulated EPR spectra of Mn(II) doped into complex **3**. The experimental spectrum was recorded at 298 K. The simulated spectrum was calculated with the following parameters: $g_{iso} = 2.00$, $A_{iso} = -0.0077$ cm^{-1}, $D = -0.2190$, $E = 0.0058$. Lower part: Angular dependence of the resonance conditions where the magnetic field is parallel to the *xz* and *yz* planes.

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Supplementary Material Available: Tables S1–S4 (anisotropic thermal parameters) and Tables S5–S8 (hydrogen atom parameters) (5 pages). Ordering information is given on any current masthead page.