Trigonal Prismatic *versus* Octahedral Co-ordination. Part 2.[1] *X*-Ray Structure Determinations of Manganese(II), Cobalt(II), and Nickel(II) Complexes of Intermediate Geometry derived from the Ligand 1,1,1-Tris(pyridine-2-aldiminomethyl)ethane

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X-Ray diffraction studies on three isomorphous divalent metal complexes (Mn, Co, and Ni) of the ligand 1,1,1-tris(pyridine-2-aldiminomethyl)ethane are reported. The sexidentate ligand has an approximate trigonal axis and defines co-ordination geometries at the metal ions which are considerably distorted from octahedral. Measures of the twisting of the ligand about the trigonal axis together with other structural parameters allow the complexes to be described in terms of a distortion towards a trigonal prismatic donor set which varies in the order $Fe^{II} < Ni^{II} < Co^{II} < Zn^{II} < Mn^{II}$. Such an order is shown to be compatible with the electronic configurations and ionic radii of the complexed metal ions.

It has been recognized recently [1-6] that a number of chelated metal ions give stable six-co-ordinate complexes in which the arrangement of the donor atoms deviates considerably from an octahedron. The description of such geometries is difficult, but in cases where the co-ordination polyhedra retain a true or pseudo-three-fold rotation axis the distorted structures may be partially characterized in terms of a twist angle ϕ between the two triangles of donors which are perpendicular to the trigonal axis (see Figure 1a). Values of 0 and 60° then define trigonal prismatic and trigonal antiprismatic arrangements of the donor atoms respectively. A second parameter (s/h, Figure 1b) allows a definition of the regularity of these extreme cases in terms of the length of the sides (s) and the distance separating (h) the two triangles of donors which are perpendicular to the three-fold axis. Thus a regular trigonal prism with square faces has $s/h = 1$, while a regular octahedron has $s/h = 1.22$.

For most of the tris(bidentate) complexes for which structural data are available the observed co-ordination geometry can be rationalized [3-6] in terms of the minimization of ligand–ligand repulsion energy.

The tris(ethane-1,2-dithiolate) complexes provide an

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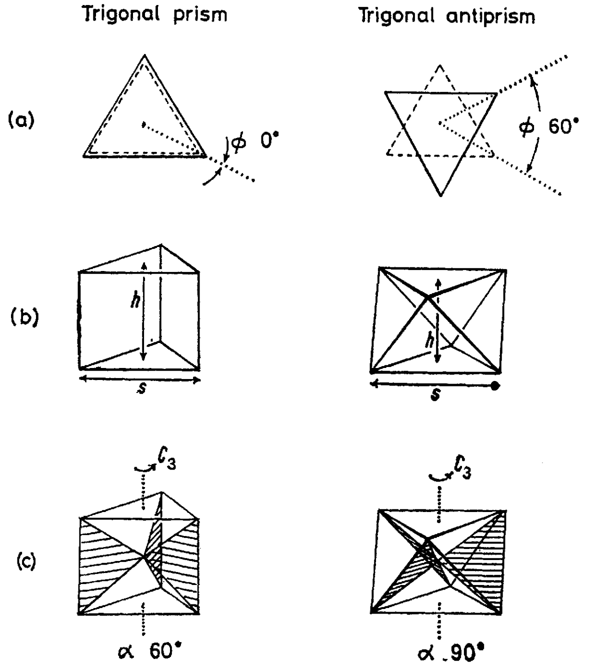


FIGURE 1 Structural parameters describing co-ordination polyhedra intermediate between a trigonal prism and antiprism: (a) trigonal twist angle ϕ, (b) compression/elongation factor s/h, and (c) dihedral angles α between bidentate co-ordination planes related by three-fold axis

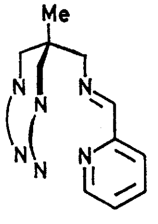
exception to this generalization, since for these dithiolate ligands 'interligand donor atom bonding' is possible and is thought [6] to favour a trigonal prismatic arrangement of the S_6^{n-} donor set. Rather surprisingly the electronic configuration of the metal ion seems to have little influence on the co-ordination geometry in all these tris(bidentate) complexes.[3,4,6]

TABLE 1

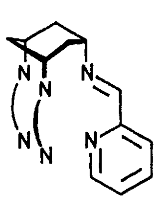
Crystallographic data for the title compounds $[M\{(py)_3tame\}][ClO_4]_2$

	Mn	Co	Ni
M	638.3	642.3	642.1
Cell constants ($P2_1/c$)			
a/Å	18.00(1)	17.92(1)	17.91(1)
b/Å	15.36(1)	15.27(1)	15.31(1)
c/Å	21.10(2)	20.01(2)	19.83(2)
β/°	151.3(2)	150.6(1)	150.4(2)
Cell constants ($P2_1/n$)			
a/Å	18.00(1)	17.92(1)	17.91(1)
b/Å	15.36(1)	15.27(1)	15.31(1)
c/Å	9.66(2)	9.83(2)	9.82(2)
β/°	92.2(3)	92.8(2)	93.9(3)
U/Å^3	2 669	2 687	2 685
D_m/g cm^{-3}	1.61	1.60	1.60
Z	4	4	4
D_c/g cm^{-3}	1.59	1.59	1.59
F(000)	1 308	1 316	1 320
μ(Mo-K_α)/cm^{-1}	7.4	8.8	9.4
Crystal size/mm	0.16 × 0.36 × 0.30	0.18 × 0.11 × 0.12	0.16 × 0.20 × 0.12
Reflections with $I \geqslant 3\sigma(I)$	1 462	1 957	2 307
Max. shift/σ	1.5	1.6	1.6
Mean shift/σ	0.4	0.2	0.3
R	0.084	0.074	0.075

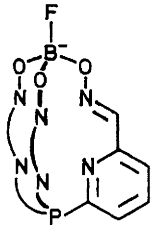
In contrast, for complexes of a number of sexidentate ligands, *e.g.* (1)—(4), the nature of the metal appears to have a significant influence on structure; for example in the first paper in this series [1] markedly different twist angles ϕ were reported for the Zn^{II} and Fe^{II} complexes of ligand (1) (28 and 43° respectively). We now report the structures of the Mn^{II}, Co^{II}, and Ni^{II} complexes in order to investigate the way in which the requirements of the metal ion determine the arrangement of the surrounding six nitrogen donors.



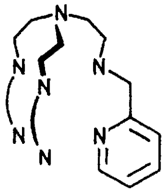
(1) $(py)_3$tame



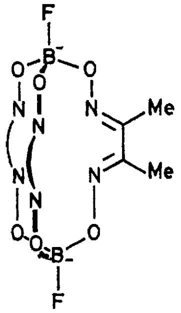
(2) $(py)_3$tach



(3) pccBF$^-$



(4) $(py)_3$tren



(5) $(dmg)_3(BF)_2^{-2}$

EXPERIMENTAL

Crystal Data.—The Mn^{II}, Co^{II}, and Ni^{II} perchlorate complexes of 1,1,1-tris(pyridine-2-aldiminomethyl)ethane were prepared as described previously [1] and single crystals suitable for X-ray diffraction studies were grown by slow evaporation of acetonitrile–ethanol (3 : 1) solutions. Weissenberg and precession photographs indicated that the three complexes were isomorphous with space group $P2_1/c$, and cell constants (Table 1) similar to those determined for the zinc complex.

For the Mn^{II} and Ni^{II} complexes data were collected on crystals mounted with the b axis coincident with the rotation axis of a Stoe–Weissenberg two-circle diffractometer, by use of zirconium-filtered Mo-K_α radiation (λ = 0.7107 Å). Unit-cell parameters were obtained from the positions of high-angle reflections and standard deviations estimated from observed and calculated values. Reflections with $\theta < 30°$ were measured in 12 layers by the ω scan technique (scan widths varying from 1 to 1.2°) at a scan rate of 1° min^{-1}. Reflections in 4 layers of crossing data were measured with similar crystals mounted on the *a* axis and these were used to scale and merge the main data according to the method of Rae.[7]

For the Co^{II} complex data were collected on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator and a scintillation counter with a peak-height analyser tuned to accept 95% of the Mo-K_α peak. 6 421 Reflections with $\theta < 30°$ were measured by the ω—2θ mode with a scan rate of $0.025° \text{ s}^{-1}$.

No evidence of decomposition was observed for any of the complexes during data collection. Lorentz and polarization corrections were applied during data processing. No corrections for absorption were attempted.

Structure Solution and Refinement.—The metal ion in each complex was assigned the same positional parameters as in the isomorphous Zn^{II} complex,[1] and the remaining non-hydrogen atoms were located from subsequent electron-density maps.

High correlations were observed in the early stages of refinement which were ascribed to the abnormally large β angles. Consequently the data were transformed to the non-standard $P2_1/n$ space group and refinement then proceeded satisfactorily to convergence (see Table 1).

The scattering factors used for all non-hydrogen atoms [8] included both real and imaginary corrections for anomalous dispersion.[9] In the final 5 cycles of refinement non-hydrogen atoms were assigned anisotropic thermal parameters and the hydrogen atoms were included in their calculated positions assuming C–H 1.0 Å and isotropic thermal parameters 10% greater than those of the adjacent carbon atoms. The hydrogen scattering factors were from ref. 10. Unit weights were used throughout.

The perchlorate anions showed high thermal parameters, but no resolvable disorder could be identified. The largest positive and negative peaks in the final electron-density difference maps existed in these regions of the unit cells: Mn 0.3 and −0.3, Co 0.2 and −0.2, and Ni 0.3 and −0.2 (*cf.* carbon *ca.* 3.0 $\text{e}\text{Å}^{-3}$). Programs used were those included in the '*X*-Ray '74' crystallographic package.[11]

Atomic positional parameters for the $P2_1/n$ cells used in refinement are listed in Table 2. Tables 3 and 4 give interatomic bond lengths and angles and selected intramolecular distances within the metal co-ordination spheres. Shortest intermolecular contacts are presented in Table 5, and the various parameters used to describe the co-ordination geometries for the metal ions for these and related complexes are included in Table 6.

The following are listed in Supplementary Publication No. SUP 21955 (44 pp., 1 microfiche)*: anisotropic thermal parameters, interatomic distances and angles, details of least-squares planes in direct space, and observed and calculated structure factors for the title complexes.

TABLE 2

Refined atomic positional parameters ($P2_1/n$ cells) and isotropic thermal parameters *

Atom	*x*	*y*	*z*	$U \times 10^2$
(*a*) Mn complex				
Mn	0.284 3(2)	0.159 2(2)	0.366 7(2)	
N(1)	0.339 8(8)	0.068 (1)	0.514 (1)	
N(2)	0.321 5(8)	0.046 (1)	0.244 (1)	
N(3)	0.373 8(9)	0.242 (1)	0.449 (1)	
N(4)	0.294 7(9)	0.266 (1)	0.211 (1)	
N(5)	0.236 6(8)	0.201 (1)	0.564 (1)	
N(6)	0.162 8(8)	0.141 (1)	0.339 (1)	
Cl(1)	0.141 0(4)	0.021 7(5)	0.850 8(6)	
O(11)	0.186 (1)	0.093 (1)	0.892 (1)	
O(12)	0.117 (1)	−0.022 (1)	0.954 (2)	
O(13)	0.086 (2)	0.048 (2)	0.763 (3)	
O(14)	0.178 (2)	−0.031 (2)	0.772 (3)	
Cl(2)	−0.452 1(4)	0.162 6(6)	0.283 9(9)	
O(21)	−0.384 (1)	0.137 (1)	0.247 (2)	
O(22)	−0.488 (1)	0.218 (2)	0.196 (2)	
O(23)	−0.495 (1)	0.104 (1)	0.337 (2)	
O(24)	−0.428 (2)	0.218 (2)	0.419 (3)	
C(1)	0.395 (1)	0.198 (1)	0.829 (2)	6.5(6)
C(2)	0.359 1(9)	0.185 (1)	0.685 (1)	3.8(4)
C(3)	0.354 (1)	0.088 (1)	0.660 (1)	4.6(5)
C(4)	0.373 (1)	0.007 (1)	0.467 (2)	5.5(5)
C(5)	0.364 (1)	−0.013 (1)	0.315 (2)	4.5(5)
C(6)	0.395 (1)	−0.083 (1)	0.256 (2)	6.6(5)
C(7)	0.380 (1)	−0.097 (1)	0.118 (2)	8.9(6)
C(8)	0.339 (1)	−0.039 (1)	0.046 (2)	8.3(6)
C(9)	0.310 (1)	0.033 (1)	0.112 (2)	5.7(5)
C(10)	0.410 (1)	0.230 (1)	0.584 (2)	5.5(5)
C(11)	0.393 (1)	0.305 (1)	0.377 (2)	5.4(5)
C(12)	0.351 (1)	0.321 (1)	0.246 (2)	5.2(5)
C(13)	0.368 (1)	0.392 (2)	0.161 (2)	7.5(6)
C(14)	0.324 (1)	0.402 (1)	0.046 (2)	7.0(6)
C(15)	0.268 (1)	0.354 (1)	0.009 (2)	6.0(5)
C(16)	0.255 (1)	0.281 (1)	0.095 (2)	5.7(6)
C(17)	0.285 (1)	0.229 (1)	0.683 (2)	5.0(5)
C(18)	0.170 (1)	0.187 (1)	0.575 (2)	4.0(4)
C(19)	0.126 (1)	0.155 (1)	0.455 (2)	4.2(4)
C(20)	0.052 (1)	0.140 (1)	0.462 (2)	6.2(6)
C(21)	0.013 (1)	0.108 (1)	0.345 (2)	6.0(6)
C(22)	0.050 (1)	0.096 (1)	0.229 (2)	5.2(5)
C(23)	0.125 (1)	0.112 (1)	0.228 (2)	5.7(6)
(*b*) Co complex				
Co	0.228 0(1)	0.160 8(1)	0.378 9(2)	
N(1)	0.336 9(5)	0.069 2(7)	0.516 7(9)	
N(2)	0.324 0(5)	0.057 4(6)	0.250 9(9)	
N(3)	0.377 8(6)	0.238 5(7)	0.445 0(9)	
N(4)	0.292 5(6)	0.260 7(7)	0.222 (1)	
N(5)	0.240 6(5)	0.208 1(7)	0.556 4(9)	
N(6)	0.171 3(5)	0.134 9(7)	0.344 (1)	
Cl(1)	0.138 8(3)	0.029 7(3)	0.8490 (4)	
O(11)	0.187 6(6)	0.097 6(8)	0.892 (1)	
O(12)	0.125 (1)	−0.029 1(9)	0.948 (1)	
O(13)	0.070 (1)	0.063 (1)	0.806 (2)	
O(14)	0.167 (1)	−0.014 (1)	0.745 (2)	
Cl(2)	−0.451 6(3)	0.155 3(4)	0.268 3(6)	
O(21)	−0.380 8(6)	0.133 1(7)	0.236 (1)	
O(22)	−0.487 7(8)	0.214 (1)	0.183 (1)	
O(23)	−0.494 5(7)	0.094 9(9)	0.321 (2)	
O(24)	−0.434 (1)	0.208 (1)	0.403 (2)	
C(1)	0.397 7(8)	0.201 (1)	0.827 (2)	6.8(4)
C(2)	0.362 8(7)	0.188 4(8)	0.682 (1)	4.7(3)
C(3)	0.351 2(7)	0.089 5(8)	0.661 (1)	4.8(3)
C(4)	0.370 4(7)	0.006 3(8)	0.465 (1)	4.8(3)
C(5)	0.362 0(6)	−0.006 3(7)	0.317 (1)	3.5(3)
C(6)	0.388 8(8)	−0.080 (1)	0.255 (1)	6.3(4)
C)7)	0.378 7(8)	−0.087 (1)	0.115 (2)	7.0(4)
C(8)	0.342 1(8)	−0.022 (1)	0.045 (1)	6.5(4)
C(9)	0.314 3(8)	0.049 0(9)	0.114 (1)	6.0(4)
C(10)	0.416 4(7)	0.225 3(9)	0.581 (1)	5.3(4)
C(11)	0.397 1(7)	0.301 9(9)	0.371 (1)	4.8(3)
C(12)	0.351 7(7)	0.314 4(9)	0.244 (1)	4.9(4)
C(13)	0.368 5(8)	0.383 (1)	0.154 (2)	7.0(4)
C(14)	0.318 7(9)	0.392 (1)	0.042 (2)	7.4(5)

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

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[11] J. M. Stewart, G. I. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, '*X*-Ray' Program System, University of Maryland, Technical Report TR-192, 1972.

Table 2 (*Continued*)

C(15)	0.260 0(8)	0.342 (1)	0.017 (1)	6.8(4)
C(16)	0.248 0(7)	0.275 0(9)	0.111 (1)	5.6(4)
C(17)	0.287 2(7)	0.237 1(8)	0.673 (1)	5.0(4)
C(18)	0.172 8(7)	0.190 2(8)	0.569 (1)	4.2(3)
C(19)	0.123 0(6)	0.154 5(8)	0.452 (1)	4.2(3)
C(20)	0.054 8(8)	0.139 4(9)	0.452 (1)	6.3(4)
C(21)	0.018 8(8)	0.101 8(9)	0.338 (1)	6.4(4)
C(22)	0.058 8(8)	0.085 8(9)	0.227 (1)	6.0(4)
C(23)	0.134 1(8)	0.101 2(9)	0.234 (1)	5.8(4)
(*c*) Ni complex				
Ni	0.288 7(1)	0.161 0(1)	0.378 6(1)	
N(1)	0.330 9(6)	0.068 9(6)	0.517 5(8)	
N(2)	0.328 4(6)	0.063 4(6)	0.251 2(8)	
N(3)	0.381 6(6)	0.230 5(6)	0.441 5(9)	
N(4)	0.288 7(6)	0.258 9(6)	0.225 4(9)	
N(5)	0.242 3(6)	0.217 1(6)	0.546 8(9)	
N(6)	0.176 5(6)	0.126 0(6)	0.345 0(9)	
Cl(1)	0.137 4(3)	0.035 9(3)	0.846 5(3)	
O(11)	0.189 2(6)	0.102 4(7)	0.891 2(9)	
O(12)	0.127 6(8)	−0.031 1(8)	0.940 (1)	
O(13)	0.065 (1)	0.074 (1)	0.825 (2)	
O(14)	0.160 (1)	0.001 (1)	0.792 (1)	
Cl(2)	−0.450 6(3)	0.151 2(3)	0.259 4(4)	
O(21)	−0.377 9(6)	0.131 5(7)	0.229 0(9)	
O(22)	−0.487 9(7)	0.210 9(9)	0.175(1)	
O(23)	−0.491 0(8)	0.084(1)	0.292 (2)	
O(24)	−0.437 (1)	0.198 (1)	0.395 (2)	
C(1)	0.400 4(8)	0.206 5(9)	0.826 (1)	5.8(4)
C(2)	0.363 5(8)	0.189 8(8)	0.679 (1)	3.9(3)
C(3)	0.354 3(8)	0.091 8(8)	0.664 (1)	4.1(3)
C(4)	0.367 7(8)	0.007 3(8)	0.470 (1)	4.2(3)
C(5)	0.361 3(8)	−0.004 4(8)	0.321 (1)	3.9(3)
C(6)	0.388 2(8)	−0.078 1(9)	0.259 (1)	5.1(4)
C(7)	0.379 8(8)	−0.083 4(9)	0.116 (1)	5.8(4)
C(8)	0.346 5(8)	−0.016 0(9)	0.046 (1)	5.2(4)
C(9)	0.322 0(8)	0.057 6(8)	0.114 (1)	4.7(4)
C(10)	0.423 4(8)	0.218 7(8)	0.577 (1)	4.5(3)
C(11)	0.399 5(8)	0.294 2(8)	0.368 (1)	3.8(3)
C(12)	0.349 6(8)	0.308 1(8)	0.244 (1)	3.9(3)
C(13)	0.367 8(9)	0.374 3(9)	0.144 (1)	5.5(4)
C(14)	0.313 8(9)	0.383 6(9)	0.035 (1)	5.9(4)
C(15)	0.253 0(8)	0.336 1(9)	0.016 (1)	5.2(4)
C(16)	0.238 8(8)	0.270 5(8)	0.117 (1)	4.3(3)
C(17)	0.293 0(7)	0.247 9(8)	0.666 (1)	3.8(3)
C(18)	0.176 6(8)	0.195 9(8)	0.563 (1)	3.6(3)
C(19)	0.133 3(7)	0.153 2(8)	0.449 (1)	3.7(3)
C(20)	0.057 0(9)	0.138 6(9)	0.443 (1)	5.6(4)
C(21)	0.019 5(9)	0.097 2(9)	0.332 (1)	6.4(4)
C(22)	0.063 7(9)	0.073 2(9)	0.227 (1)	6.0(4)
C(23)	0.139 0(9)	0.088 2(8)	0.236 (1)	4.7(4)

* Estimated standard deviations in this and subsequent Tables are given in parentheses. Anisotropic thermal parameters are included in the Supplementary Publication (see footnote to text).

RESULTS AND DISCUSSION

The Mn^{II}, Co^{II}, and Ni^{II} ions in the three isomorphous complexes of 1,1,1-tris(pyridine-2-aldiminomethyl)ethane exist in discrete cationic complexes, and are well-separated from the perchlorate counter ions. There are no abnormally short intermolecular contacts. The shortest (Table 5) involve the approach of perchlorate oxygen atoms to hydrogen atoms in the ligands. The co-ordination polyhedra of the metal ions are irregular and vary significantly from one complex to another. The disposition of the sexidentate ligand about the metal and the atom labelling scheme used are shown for the manganese complex in Figure 2; Figure 3 shows the twisting of the ligand.

There are no unusual features associated with the bond distances in the ligands in each of the three structures. Mean bond lengths are: C_{sp^3}–C_{sp^3} 1.53(2), C_{sp^2}–C_{sp^2} 1.38(4), methylene C–N 1.47(2), C=N(imine) 1.25(2), and C=N(py) 1.34(2) Å. Equivalent bonds in the ligands in the different complexes have the same lengths in all cases except for N(1)–C(3), N(5)–C(17), and C(2)–C(10).

Table 3

Interatomic bond lengths (Å) and angles (°) in the co-ordination sphere of the complexes

Metal	Mn	Co	Ni
(*a*) Distances			
M–N(1)	2.209 (15)	2.108 (9)	2.069 (9)
M–N(2)	2.220 (15)	2.138 (9)	2.105(9)
M–N(3)	2.179 (16)	2.079 (10)	2.035 (10)
M–N(4)	2.240 (16)	2.170 (10)	2.126 (9)
M–N(5)	2.222 (14)	2.104(10)	2.085 (10)
M–N(6)	2.211 (14)	2.139 (9)	2.085 (10)
(*b*) Angles			
N(1)–M–N(2)	73.3(5)	76.1(4)	77.6(3)
N(1)–M–N(3)	79.8(6)	83.5(4)	84.3(4)
N(1)–M–N(4)	148.3(6)	153.2(4)	158.5(4)
N(1)–M–N(5)	78.9(5)	82.4(4)	84.5(4)
N(1)–M–N(6)	114.7(5)	110.6(4)	103.5(4)
N(2)–M–N(3)	114.6(6)	110.7(4)	104.4(4)
N(2)–M–N(4)	100.3(5)	94.5(4)	93.6(4)
N(2)–M–N(5)	145.3(5)	152.5(4)	159.0(4)
N(2)–M–N(6)	98.8(5)	95.2(4)	94.8(4)
N(3)–M–N(4)	74.8(5)	76.4(4)	78.9(4)
N(3)–M–N(5)	79.6(5)	83.2(4)	84.6(4)
N(3)–M–N(6)	146.3(6)	153.1(4)	160.4(4)
N(4)–M–N(5)	114.2(6)	112.1(4)	106.9(4)
N(4)–M–N(6)	96.8(5)	95.0(4)	96.7(4)
N(5)–M–N(6)	74.2(5)	76.4(4)	78.4(4)

In each complex, as in the previously determined structures [1] for the Fe^{II} and Zn^{II} complexes, the triangle defined by the aldimino-donors [N(1), N(3), and N(5)] is almost parallel to the triangle of pyridino-donors [N(2), N(4), and N(6)] (Table 6). These triangles are almost equilateral in every case (Table 4) and the metal ions lie close to a line joining their centroids.

Table 4

Selected intramolecular non-bonded contacts (Å)

Metal	Mn	Co	Ni
N(1) ··· N(3)	2.82(2)	2.78(1)	2.76(1)
N(1) ··· N(5)	2.82(2)	2.77(1)	2.79(1)
N(3) ··· N(5)	2.82(2)	2.77(1)	2.77(1)
N(1) ··· N(2)	2.64(2)	2.59(1)	2.62(1)
N(3) ··· N(4)	2.68(2)	2.60(1)	2.64(1)
N(5) ··· N(6)	2.67(2)	2.60(1)	2.64(1)
N(2) ··· N(4)	3.42(2)	3.16(1)	3.08(1)
N(2) ··· N(6)	3.37(2)	3.16(1)	3.09(1)
N(4) ··· N(6)	3.33(2)	3.17(1)	3.14(1)

Under these circumstances it is possible [12,13] to consider a description of the co-ordination polyhedron in terms of a twist angle between these triangular faces. Various methods for calculating such angles have been suggested.[12,13] Method (1) of Table 6 involves the projection of the six donor atoms N(1)—(6) on the plane containing the metal atom which lies perpendicular to the line joining the centroids of the triangular faces.

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[12] K. R. Dymock and G. J. Palenik, *Inorg. Chem.*, 1975, **14**, 1220.

[13] M. A. Flandera and E. C. Lingafelter, *Inorg. Chem.*, 1976, **15**, 750.

The angles ϕ_{12} *etc.* are those subtended at the metal ion by the projected atoms N(1′) and N(2′), *etc.* In method (2) the metal atom and N(1), N(3), and N(5) are projected on the plane defined by N(2), N(4), and N(6). ϕ_{12} is then the angle subtended at the projected metal ion by N(2) and the projected atom N(1′). Method (3) is similar to method (2) except that the projections are made on the N(1), N(3), N(5) plane.

TABLE 5

Shortest intermolecular contacts (<2.5 Å), excluding interhydrogen contacts

Metal	Mn	Co	Ni
$O(11)\cdots H(9^{I})$	2.2	2.3	2.4
$O(11)\cdots H(23^{I})$	2.4		
$O(14)\cdots H(14^{II})$		2.2	2.1
$O(21)\cdots H(8^{III})$	2.5	2.5	2.5
$O(22)\cdots H(20^{IV})$	2.4	2.4	2.4
$O(23)\cdots H(4^{V})$	2.2	2.2	2.3

* Hydrogen atoms are assigned the same number as the carbon atom to which they are bonded. Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $x, y, 1 + z$
II $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$
III $\bar{x}, \bar{y}, \bar{z}$
IV $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
V $\bar{x}, \bar{y}, 1 - z$

The three methods give mean twist angles ($\bar{\phi}$) which agree closely. However, method (1) gives less variation of the individual twist angle from the mean in every case, and we would therefore concur with the recommendation of Flandera and Lingafelter[13] that this definition of twist angle (ϕ^{i}_{11} of the possibilities they considered and ϕ_{i}^{4} of the possibilities examined by Dymock and Palenik[12]) be used for such co-ordination polyhedra.

TABLE 6

Parameters defining the co-ordination polyhedra in the $[M\{(py)_3tame\}][ClO_4]_2$ complexes

(*a*) Twist angles/°		Mn	Zn	Co	Ni	Fe
Method (1)	ϕ_{12}	20.6	27.8	28.0	35.5	43.0
	ϕ_{34}	23.0	27.5	28.1	36.8	44.5
	ϕ_{56}	21.5	28.2	28.1	37.3	42.7
Mean	$\bar{\phi}$	21.7	27.8	28.1	36.5	43.4
		(1.2) [a]	(0.4)	(0.1)	(0.9)	(1.0)
Method (2)	$\bar{\phi}$	22.0	27.8	28.0	36.3	43.4
		(2.3)	(0.9)	(1.4)	(1.3)	(2.9)
Method (3)	$\bar{\phi}$	22.0	27.9	28.0	36.3	43.4
		(1.4)	(1.6)	(1.3)	(1.7)	(3.4)
(*b*) Triangular faces N(1), N(3), N(5) and N(2), N(4), N(6) [b]						
Inclination/°		1.0	0.9	0.7	1.3	0.9
h/Å		2.560 [c]	2.510	2.479	2.404	2.245
s_{ald}(mean)/h		1.101 [c]	1.119	1.121	1.152	1.171
s_{py}(mean)/h		1.318 [c]	1.291	1.279	1.290	1.296
(*c*) Inclination between chelating arms [b]						
α(mean)/°		66.1 [c]	69.3	69.4	74.9	79.8

[a] Standard deviation of the mean in parentheses. [b] Equations of planes are given in Supplementary Publication. [c] See Figure 1b and 1c for definition of these parameters; ald and py refer to the triangles of aldimino- and pyridino-donors, respectively and h is the distance between the centroids of the triangles.

The compression/elongation parameter (Figure 1b) commonly used to describe the co-ordination geometry of tris(bidentate) chelates[3,6] is less useful for these sexidentate complexes because the values of s are different for the aldimino- and pyridino-nitrogen triangles in each complex. In all cases the triangle of pyridine nitrogen atoms is larger than that of the imine nitrogen atoms. Similar ' tapering ' of the co-ordination polyhedra has been reported previously.[1,14] Despite this difficulty the expected compression of the polyhedra with increasing ϕ is illustrated by the monotonic decrease in h and increase in s_{ald}/h (see Table 6).

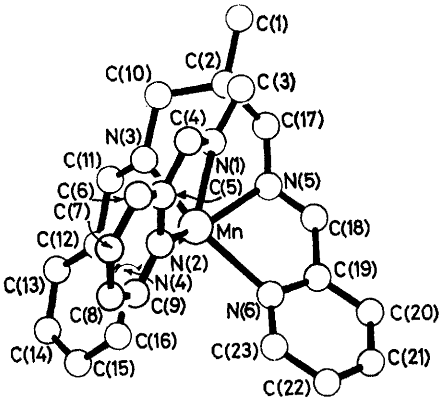

FIGURE 2 The structure of the $[Mn\{(py)_3tame\}]$ dication, showing the atom labelling scheme used for the ligand

The three co-ordination planes [M, N(1), N(2); M, N(3), N(4); and M, N(5), N(6)] defined by the arms of the ligand related by the pseudo three-fold axis will be inclined at angles to each other (α) of 60 and 90° in the prismatic and antiprismatic forms of the polyhedra respectively (see Figure 1c). The values of $\bar{\alpha}$ increase monotonically with $\bar{\phi}$ as expected.

From Table 6 the order of increasing tendency to adopt a trigonal antiprismatic geometry is: $Mn^{II} < Zn^{II} < Co^{II} < Ni^{II} < Fe^{II}$. The differences in the co-ordination polyhedra are large and, unlike the situations in complexes of related sexidentate ligands (see Table 7),[1,5,14-17] the limiting cases of the trigonal prism or trigonal antiprism are not approached by any members of the series.

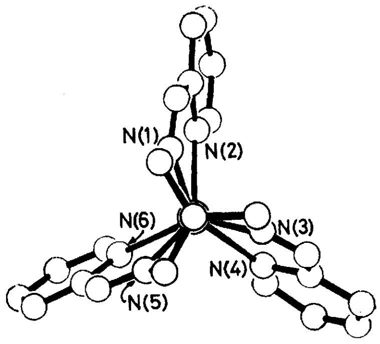

FIGURE 3 The structure of the $[Mn\{(py)_3tame\}]$ dication, showing the twisting of the ligand about the pseudo-three-fold axis through the metal, C(2), and C(1) atoms

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[14] W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Comm.*, 1969, 843.

[15] M. R. Churchill and A. H. Reis, *Inorg. Chem.*, 1972, **11**, 1811, 2299; 1973, **12**, 2280; *J.C.S. Dalton*, 1973, 1570.

[16] G. A. Zakrzewski, C. A. Ghilardi, and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1971, **93**, 4411.

[17] C. Mealli and E. C. Lingafelter, *Chem. Comm.*, 1970, 885.

The effects of differences in ligand structures may be compared from the data in Table 7. It is now possible to confirm that for a given metal ion the tendency for the ligands (**1**)—(**5**) to adopt a trigonal prismatic donor set decreases with the rigidity of the ligand in the order:[1] $[\mathrm{pccBF}]^- > [(\mathrm{dmg})_2(\mathrm{BF})_2]^{2-} > \{(\mathrm{py})_3\mathrm{tach}\} > \{(\mathrm{py})_3\mathrm{tame}\} > \{(\mathrm{py})_3\mathrm{tren}\}$.

In an attempt to predict how the nature of the metal ion will influence the geometry of such complexes, calculations have been performed[2,5] to determine the effect of the changing the arrangement of the donor atoms on the ligand-field stabilization energy (LFSE) for different *d*-electron configurations. A simplified ionic model has allowed[2] the calculation of the difference in LFSE between regular octahedral and trigonal prismatic arrangements of otherwise identical donor sets, and predicts a preference for an octahedral geometry in the order: $\mathrm{Mn^{II}(h.s.)} = \mathrm{Zn^{II}} < \mathrm{Co^{II}(h.s.)} < \mathrm{Ni^{II}} < \mathrm{Fe^{II}(l.s.)}$ for the metals and spin states[1] considered here. A more detailed treatment,[5] which takes into account how the LFSE varies with ϕ for different 'bite' angles defined by the chelating arms of the ligands, gives the same series (**3**) for the particular case of bite angles of 77° (close to those observed for the present structures, see Table **3**).

TABLE 7

Mean twist angles, ϕ, in complexes of related sexidentate nitrogen ligands

M	$\mathrm{Fe^{II}}$	$\mathrm{Co^{III}}$	$\mathrm{Co^{II}}$	$\mathrm{Ni^{II}}$	$\mathrm{Zn^{II}}$
$[\mathrm{M(pccBF)}][\mathrm{BF_4}]$ [a]	22		1.2	1.6	1.9
$[\mathrm{M\{(dmg)_3(BF)_2\}}]^{z+}$		31.2 [b]	8.6 [c]		
$[\mathrm{M\{(py)_3tach\}}]$-$[\mathrm{ClO_4}]_2$ [d]			32	4.6	
$[\mathrm{M\{(py)_3tame\}}]$-$[\mathrm{ClO_4}]_2$ [e]	43		29	36	28
$[\mathrm{M\{(py)_3tren\}}]^{2+}$ [f]	54 [g]		49 [h]	51 [i]	46

[a] Ref. 15. [b] $z = 1$, Anion $[\mathrm{BF_4}]^-$, ref. 16. [c] $z = 0$, ref. 16. [d] Refs. 1 and 14. [e] This work. [f] Refs. 5 and 17. [g] Anion $[\mathrm{BF_4}]^-$. [h] Anion unspecified. [i] Anion $[\mathrm{PF_6}]^-$.

For the $[\mathrm{M\{(py)_3tame\}}]^{2+}$ complexes the agreement between the calculated and the observed series order is good except that significantly different geometries are observed for the $\mathrm{Zn^{II}}$ and high-spin $\mathrm{Mn^{II}}$ complexes, despite the fact that these both show zero LFSE in all fields. An explanation of this discrepancy can be given in terms of the variation of effective ionic radius of the metal ions, which could not be considered[5] in the calculations due to the numbers of parameters involved.

It can be shown geometrically[5] that $\cos(\phi/2) = [3a^2 - \frac{3}{4}b^2]^{\frac{1}{2}}/s$ where a is the metal–ligand distance, b the chelate 'bite' in the limbs related by the three-fold axis, and ϕ and s are as defined previously. Thus, for a series of complexes with the same values of s and b, a larger ϕ angle will be expected for a metal with a smaller ionic radius, since this should lead to a decrease in a.*

This equation cannot be used to relate quantitatively changes in ϕ with ionic radius of M in $[\mathrm{M\{(py)_3tame\}}]^{2+}$ because of the tapering of the polyhedron already described. However, for a complex with D_3 symmetry having ϕ, a, and b values as those for the Mn complex, a decrease in a of 0.07 Å (the difference between the ionic radii of $\mathrm{Mn^{II}}$ and $\mathrm{Zn^{II}}$)[18] should increase ϕ by 37° if the ligand were capable of responding fully to the resulting changes in optimum metal–donor distances, a. This predicted difference in ϕ for the Zn and Mn complexes is much greater than that observed (6°) for the $\{(\mathrm{py})_3\mathrm{tame}\}$ complexes, but does suggest that relatively small changes in ionic radii of the metals will account adequately for significant differences in the structures of their co-ordination polyhedra.

The results of these studies allow us to conclude that a consideration of both LFSE terms and the effects of variation of ionic radii is necessary to interpret the differences in co-ordination geometries of complexes which are intermediate between a trigonal prism and an octahedron. They also emphasize the inappropriateness of assuming that a series of isomorphous complexes will be isostructural.

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[6/1690 *Received, 6th September*, 1976]

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* Refs. 3, 4, and 6 contain analyses of the effects of variation of b/a values on ϕ for tris(bidentate) chelates.

[18] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1969, **B25**, 925.