

Effects of d -orbital occupancy on the geometry of the trigonal–bipyramidal complexes $[M^{II}Cl_3(Hdabco)(dabco)]_n$, where M is Mn, Co, Ni or Cu and dabco is 1,4-diazabicyclo[2.2.2]octane

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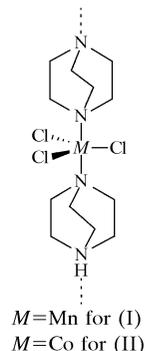
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Geometric data from (1-aza-4-azoniabicyclo[2.2.2]octane- κN^1)(1,4-diazabicyclo[2.2.2]octane- κN^1)trichloromanganese(II), $[MnCl_3(C_6H_{13}N_2)(C_6H_{12}N_2)]$ or $[MnCl_3(Hdabco)(dabco)]$ (dabco is 1,4-diazabicyclo[2.2.2]octane), and the cobalt(II) analogue, $[CoCl_3(C_6H_{13}N_2)(C_6H_{12}N_2)]$, have been combined with previously reported data for the Ni and Cu analogues to show that bond-length trends across the isotypal series are consistent with a high-spin trigonal–bipyramidal system. As each transition metal is positioned on a D_3 site in the space group $R32$ (No. 155), two bond lengths fully define each trigonal–bipyramidal coordination geometry [$Mn-Cl = 2.3903$ (7) Å and $Mn-N = 2.367$ (2) Å, and $Co-Cl = 2.3080$ (8) Å and $Co-N = 2.269$ (3) Å].

Comment

Comparison of bond lengths in transition metal compounds shows that imperfect shielding of metal nuclei by d electrons leads to a general contraction across a series. This trend is reversed at points where d orbitals that coincide with bonds are occupied. The above effects were noted for octahedral metal oxides by van Santen & van Wieringen (1952) and demonstrated more recently for a series of octahedral complexes by Cotton *et al.* (1984, 1993). The latter compounds also show evidence of Jahn–Teller distortion. Chemists usually describe the above effects in terms of crystal- or ligand-field theories, which attempt to quantify the energy cost of placing an electron in a bonding d orbital (*e.g.* for an octahedral complex, the d orbitals divide into high-energy $d_{x^2-y^2}$ and d_{z^2} , directed along the bonds, and lower-energy d_{xy} , d_{xz} and d_{yz} , projecting between the bonds). Importantly, the energy gap between the two sets of orbitals determines whether it is energetically favourable to pair electrons in the lowest-energy

orbitals or to semi-fill all five d orbitals before starting to pair electrons (*i.e.* low-spin *versus* high-spin configurations).



The same rationale can be used for analysing the title trigonal–bipyramidal (tbp) structures, $[M^{II}Cl_3(Hdabco)(dabco)]_n$, where M is Mn, Co, Ni or Cu and dabco is 1,4-diazabicyclo[2.2.2]octane. The Mn and Co structures, (I) and (II), from the current study (Fig. 1) form an isotypal series with the previously reported Ni (Petrusenko *et al.*, 1997) and Cu analogues (Karan *et al.*, 1999; Viossat *et al.*, 1988). In the tbp geometry, the five d orbitals divide into three subsets, *viz.* low-energy d_{xz} and d_{yz} , medium-energy d_{xy} and $d_{x^2-y^2}$, lying in the same plane as the three equatorial $M-Cl$ bonds, and high-energy d_{z^2} , pointing directly along the axial $M-N$ bonds. When the crystallographically determined $M-Cl$ and $M-N$ bond lengths are plotted against d -electron configuration (Fig. 2), the curves diverge at Ni^{II} . This is as expected for a high-spin tbp system. All bonds contract as electrons fill non-bonding d_{xz} and d_{yz} orbitals in the d^5 to d^7 configurations, but occupation of equatorial d_{xy} and $d_{x^2-y^2}$ in d^8 and d^9 causes the $M-Cl$ bonds to lengthen, whilst allowing the $M-N$ bonds to continue contracting. The $M-N$ bonds would not be expected to expand until all five d orbitals are fully occupied. Support for the high-spin assignment is obtained from the tbp compounds $[M^{II}Cl_3(dabcoH)_2]$ ($M = Mn, Fe, Ni$ and Cu),

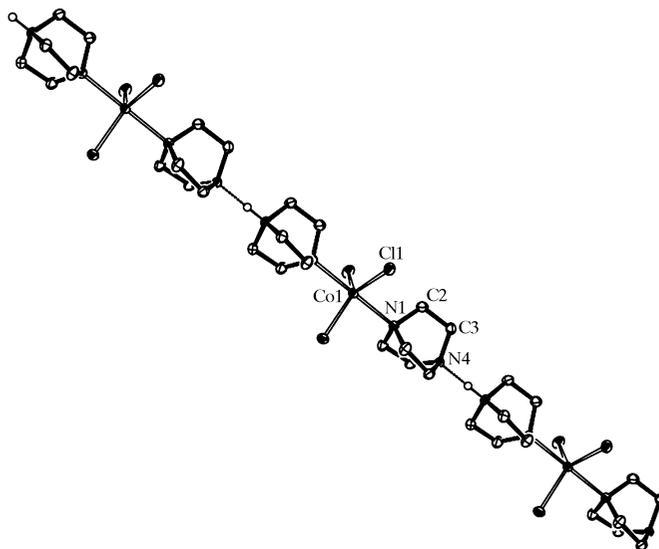


Figure 1
A view of $[Co^{II}Cl_3(Hdabco)(dabco)]_n$ (50% probability displacement ellipsoids). Most H atoms have been omitted for clarity.

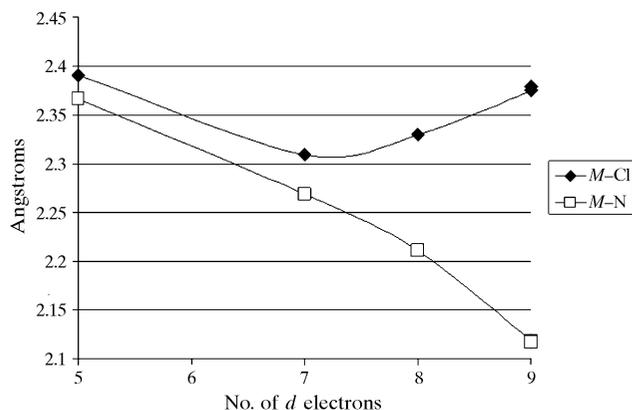


Figure 2
A plot of *M*–Cl and *M*–N bond lengths (Å) versus *d*-electron configuration in $[M^{II}Cl_3(Hdabco)(dabco)]_n$, where *M* is Mn and Co (current work), Ni (Petrusenko *et al.*, 1997), and Cu (Viossat *et al.*, 1988; Karan *et al.*, 1999). The *M*–Cl and *M*–N s.u. values are in the ranges 0.0007–0.002 and 0.002–0.006 Å, respectively.

which were previously classified as high-spin based on spectroscopic studies (Vallarino *et al.*, 1972).

It is likely that Jahn–Teller distortion of the Ni–Cl bonds has been masked by the crystallographic threefold axis. Previous structural studies of $[M^{II}Cl_3(CH_3dabco)_2]ClO_4$ (*M* = Ni and Cu; Rozell & Wood 1977), where all the bonds are crystallographically independent, showed a small but significant deformation in the d^8 Ni complex. The dabco dimensions in the title Mn and Co structures show good agreement and are as expected (Tables 1 and 2). Interestingly, the *M*–N bonds are aligned with the crystal *c* axis in the current structures so that variations in unit-cell dimensions mirror changes in bond lengths. This suggests that spectroscopic excitation of *d* electrons may well have a macroscopic effect and that these materials should be investigated for opto-mechanical uses.

Experimental

Crystals of the title Mn and Co compounds were prepared by mixing equal volumes of 0.2 *M* methanol solutions of dabco and *MCl*₂. Long needles, suitable for crystallographic investigation, formed when these solutions were subjected to vapour diffusion using diethyl ether as the anti-solvent.

Compound (I)

Crystal data

$[MnCl_3(C_6H_{13}N_2)(C_6H_{12}N_2)]$ $D_x = 1.585 \text{ Mg m}^{-3}$
 $M_r = 386.65$ Mo $K\alpha$ radiation
 Hexagonal, *R*32 $\mu = 1.31 \text{ mm}^{-1}$
 $a = 10.601(2) \text{ \AA}$ $T = 223(2) \text{ K}$
 $c = 12.484(2) \text{ \AA}$ Needle, colourless
 $V = 1215.0(4) \text{ \AA}^3$ $0.3 \times 0.1 \times 0.1 \text{ mm}$
 $Z = 3$

Data collection

Enraf–Nonius CAD-4 diffractometer 487 independent reflections
 Non-profiled $\omega/2\theta$ scans 480 reflections with $I > 2\sigma(I)$
 Absorption correction: ψ scan $R_{int} = 0.019$
 (North *et al.*, 1968) $\theta_{max} = 25.0^\circ$
 $T_{min} = 0.696$, $T_{max} = 0.881$ 3 standard reflections
 1514 measured reflections frequency: 60 min
 intensity decay: 2%

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0248P)^2]$
 $R[F^2 > 2\sigma(F^2)] = 0.015$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.037$ $(\Delta/\sigma)_{max} = 0.001$
 $S = 1.07$ $\Delta\rho_{max} = 0.16 \text{ e \AA}^{-3}$
 487 reflections $\Delta\rho_{min} = -0.13 \text{ e \AA}^{-3}$
 50 parameters Extinction correction: *SHELXL97*
 H atoms treated by a mixture of independent and constrained refinement Extinction coefficient: 0.0011 (4)
 Absolute structure: Flack (1983),
 201 Friedel pairs
 Flack parameter: 0.01 (2)

Table 1

Selected geometric parameters (Å, °) for (I).

Mn1–N1	2.367 (2)	C2–C3	1.537 (2)
Mn1–Cl1	2.3903 (7)	C3–N4	1.4806 (16)
N1–C2	1.4717 (18)		
C2–N1–C2 ⁱ	108.23 (10)	N4–C3–C2	108.96 (12)
N1–C2–C3	110.77 (13)	C3–N4–C3 ⁱ	108.97 (9)

Symmetry code: (i) $-y + 2, x - y + 1, z$.

Compound (II)

Crystal data

$[CoCl_3(C_6H_{13}N_2)(C_6H_{12}N_2)]$ $D_x = 1.644 \text{ Mg m}^{-3}$
 $M_r = 390.64$ Mo $K\alpha$ radiation
 Trigonal, *R*32 $\mu = 1.59 \text{ mm}^{-1}$
 $a = 10.5409(10) \text{ \AA}$ $T = 223(2) \text{ K}$
 $c = 12.303(2) \text{ \AA}$ Needle, blue
 $V = 1183.9(2) \text{ \AA}^3$ $0.25 \times 0.1 \times 0.05 \text{ mm}$
 $Z = 3$

Data collection

Enraf–Nonius CAD-4 diffractometer 1463 measured reflections
 Non-profiled $\omega/2\theta$ scans 470 independent reflections
 Absorption correction: ψ scan 457 reflections with $I > 2\sigma(I)$
 (North *et al.*, 1968) $R_{int} = 0.029$
 $T_{min} = 0.692$, $T_{max} = 0.925$ $\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0197P)^2]$
 $R[F^2 > 2\sigma(F^2)] = 0.020$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.041$ $(\Delta/\sigma)_{max} < 0.001$
 $S = 1.1$ $\Delta\rho_{max} = 0.15 \text{ e \AA}^{-3}$
 470 reflections $\Delta\rho_{min} = -0.16 \text{ e \AA}^{-3}$
 50 parameters Extinction correction: *SHELXL97*
 H atoms treated by a mixture of independent and constrained refinement Extinction coefficient: 0.0006 (3)
 Absolute structure: Flack (1983),
 194 Friedel pairs
 Flack parameter: 0.00 (2)

Table 2

Selected geometric parameters (Å, °) for (II).

Co1–N1	2.269 (3)	C2–C3	1.528 (3)
Co1–Cl1	2.3080 (8)	C3–N4	1.482 (3)
N1–C2	1.472 (3)		
C2–N1–C2 ⁱ	107.60 (16)	N4–C3–C2	109.0 (2)
N1–C2–C3	111.3 (2)	C3–N4–C3 ⁱ	108.62 (14)

Symmetry code: (i) $-y, x - y, z$.

Final refinements of both structures were carried out in the space group *R*32 (No. 155) with all non-H atoms anisotropic and H atoms isotropic, except for amine atom H4, whose $U_{iso}(H)$ value was fixed at 0.028 (Mn) or 0.025 Å² (Co) due to the close proximity of a disordered symmetry-related position. In this space group, a disordered

amine H atom semi-populates two sites on the threefold axis between adjacent N atoms. As previous refinements of the Cu analogue were carried out in both *R32* and *R3* (No. 146), which gave an improved description of the amine H atom, refinements of the current structures were also attempted in *R3*. However, as the amine H atoms remained disordered, the *R3* refinements were discontinued. The choice of space group made negligible difference to the *M*–Cl and *M*–N bond lengths.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) for (I) and *SHELXS97* (Sheldrick, 1997) for (II); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3016). Services for accessing these data are described at the back of the journal.

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