DALTON

The design of a new type of very rigid tetradentate ligand ‡

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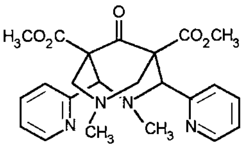
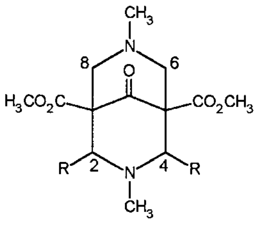
Molecular mechanics calculations were used to compute the structural properties of a new type of very rigid tetradentate ligand for tetrahedral co-ordination geometries. The calculations indicate that the pendant arms of the disubstituted bispidine (3,7-diazabicyclo[3.3.1]nonane) backbone need to form six-membered chelate rings with the metal to allow a distorted tetrahedral geometry. Smaller rings lead to five- (trigonal bipyramidal) or six-co-ordinate (octahedral) transition-metal compounds. The quality of these predictions is supported by the experimentally determined structure of a cobalt(II) compound of the ligand with co-ordinated pyridine substituents (five-membered chelate rings) and an additional bidentate nitrate ligand. Comparison of the computed structures with the crystal structure of the cobalt(II) compound and with that of a ligand with methyl-protected phenyl substituents supports the rigidity of the bispidine backbone and indicates that rotation of co-ordinating side chains around a C–C single bond is the only flexibility in these ligands.

Enforced co-ordination geometries can stabilize unusual electronic structures of transition-metal ions with specific spectroscopic, magnetic and redox properties. Rigid ligands can also affect the stability of metal complexes and thus lead to high metal-ion selectivity.[1] Macrocyclic and sterically reinforced ligands have been used as metal-ion-selective complexing agents.[1,2] There are many reasons for a strong interest in ligands enforcing specifically a tetrahedral co-ordination geometry. (*i*) The stability of first-row transition-metal complexes generally follows the Irving–Williams series,[3] and size-matching as well as sterically reinforced macrocyclic ligands have not really been able to modify this sequence so far. Enforced tetrahedral co-ordination was thought to be able to overcome this problem.[4] However, ligands that have been designed based on these ideas have, so far, not been able to enforce tetrahedral geometries upon metal ions other than zinc(II). (*ii*) The kinetic and thermodynamic electron-transfer properties of metalloprotein redox couples are modulated by the rigidity of the protein backbone. The rather high potentials and fast electron-exchange rates of the blue copper proteins are, to some extent, due to the enforced trigonal-pyramidal (sometimes erroneously termed 'tetrahedral') geometry.[5] (*iii*) Tetrahedral ligand fields are weaker than octahedral ligand fields and, generally, tetrahedrally co-ordinated metal ions therefore have high-spin electronic configurations, even when a spin equilibrium would theoretically be possible. The design of ligands enforcing tetrahedral co-ordination with short metal-donor distances is also attractive in this context.

To enforce highly strained co-ordination geometries, the ligand backbone must be very rigid. Substituted bispidine (3,7-diazabicyclo[3.3.1]nonane) and bispidone molecules are tetradentate compounds with such a structure. Substitution on the nitrogen donors in the bispidine framework with co-ordinating side chains has been used to enforce square-planar geometry.[6] The bispidine group is based on two six-membered rings, and the most stable geometry is the chair/chair conformation with C(2) and C(4) substituents in an equatorial configuration (L^1). This also follows from published experimental data.[7] Thus, the only possible reorganization in this type of compound, required prior to co-ordination in a tetradentate manner, is a rotation around the C(2)–R and the C(4)–R bonds. Note, that therefore it is not necessarily warranted to call these compounds tetrahedrally preorganized. By varying the substituents in the C(2) and C(4) positions, with pendant arms of different size, shape and steric demand, and with varying donor atoms, different co-ordination geometries may be obtained (tetrahedral, trigonal bipyramidal and octahedral), allowing the tuning of physical properties of the corresponding metal complexes.



L^1



In this publication we present our molecular mechanics studies on the design of this new type of ligand, supported by experimentally determined structures of a derivative of a metal-free compound and of a cobalt(II) compound of a bispidone derivative which was predicted and observed to lead to a six-co-ordinate structure.

Results and Discussion

Molecular modelling

Molecular mechanics calculations, using an established force field,[8–10] were carried out to determine the rigidity of C(2)- and C(4)-substituted bispidine type compounds. The force field used is rather conventional, except that the angular geometry is modelled by 1,3-non-bonded interactions,[9] and the parameters used have been validated in many studies. The recently developed approach,[10] using a small perturbation of this model, with a harmonic sine function and a ligand-field-based generic force constant, was not used here since the gain in accuracy for cobalt(II) (high spin d^7) is minimal, and since this approach would not have allowed us to compute metal-ion-independent strain-energy curves.

Cobalt(II) complexes of the ligands with five- or six-membered chelate rings, pyridine donors in the side chains, and ammonia as an additional ligand, leading to four-, five-, or six-co-ordinate compounds, were refined. A four-co-ordinate

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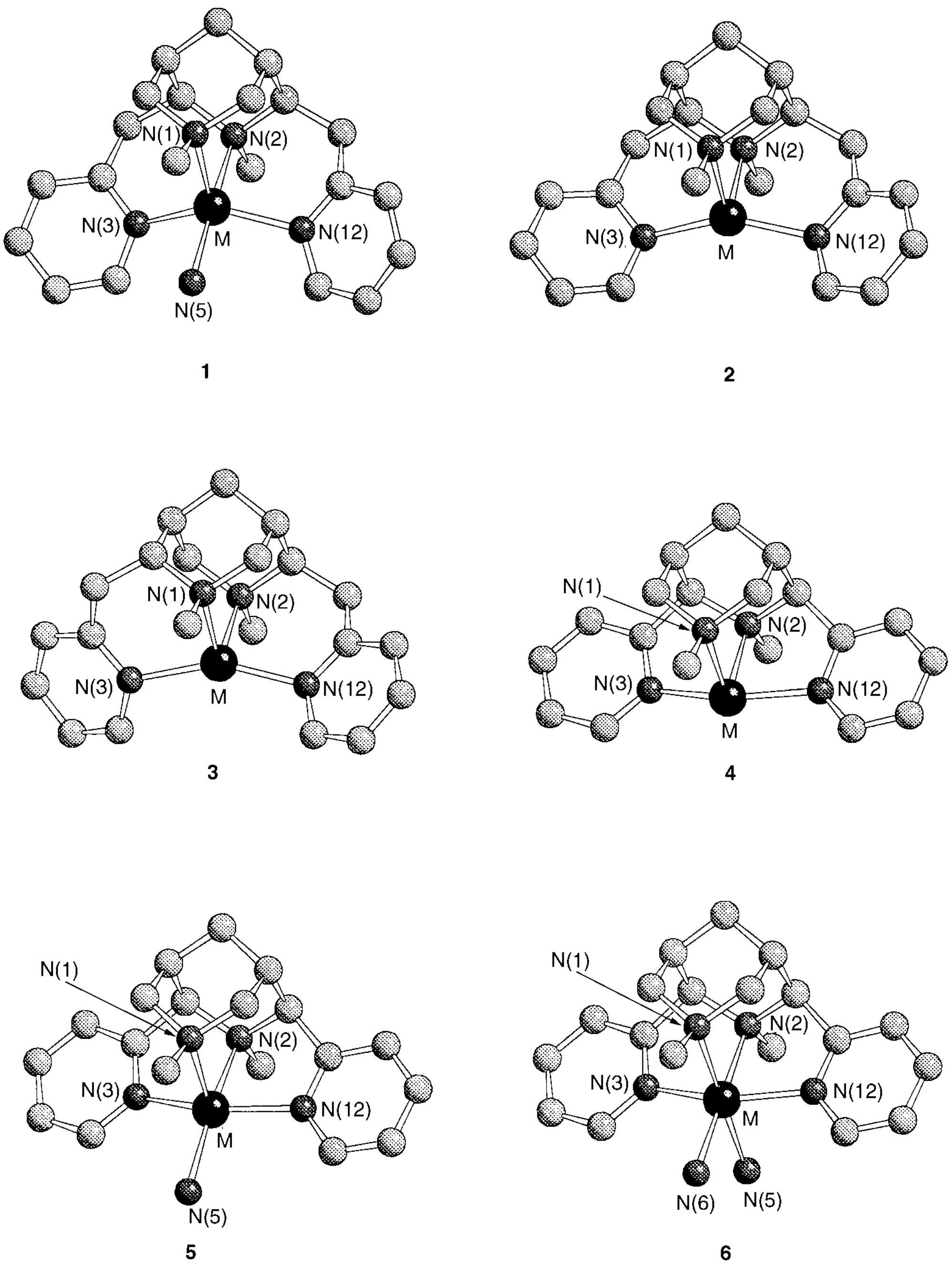
‡ *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.



1 2 3 4 5 6

Fig. 1 The SCHAKAL[11] plots of the strain-energy-minimized structures of six cobalt(II) bispidine complexes (**1-3**, six-membered chelate rings involving the pyridine donors; **4-6**, five-membered chelate rings; **3**, *trans* configuration of the bispidine ligand; for structural parameters and strain induced to the ligand backbone, see Table 1)

cobalt(II) compound with a bispidine type ligand having a methano spacing group between the backbone and the pyridine substituents (six-membered chelate rings) of *trans* configuration [substituents of C(2) and C(6) positions; see L^1 above; structure **3** in Fig. 1 and Table 1] was also refined. This structure is, in terms of the distorted-tetrahedral co-ordination geometry, rather similar to that of the ligand with *cis*-configurated pendant groups (structure **2**). For this reason, and because our preparative work was based on compounds with *cis* configuration, further studies with *trans*-substituted bispidine ligands were not pursued. The optimized structures can be seen in Fig. 1, which also gives the nomenclature used in Table 1 and in the text, and the metal–donor distances, valence angles around the metal centre and the strain energies induced to the bispidine-type ligands (see below) are given in Table 1. Table 1 also includes the corresponding structural data for a metal-free bispidine derivative (crystal structure), and for a six-co-ordinated cobalt(II) complex with a five-membered chelate ring derivative of bispidine and a co-ordinated bidentate nitrate (X-ray and molecular mechanics refined structure).

Two comments regarding these studies are required here. (*i*) Ammonia was used as an additional monodentate ligand to complete the co-ordination sphere for the five- and six-co-ordinate species, instead of nitrate or chloride, which was co-ordinated in the two experimentally characterized cobalt(II) complexes, or OH_2, which might co-ordinate in aqueous solution. The main reason is that our cobalt(II)–amine force field has been extensively tested and therefore was expected to lead to the most reliable results. The assumption that the nature of the extra ligand is not of major importance for the structure and the strain of the central four-co-ordinate core and the bispidine-type ligand backbone has been tested by refining the structure of the six-co-ordinate species with a cobalt(II)–nitrate group constrained to the experimentally determined geometry. For this reason, the coordinates of cobalt, the nitrate nitrogen and the three nitrate oxygen atoms were fixed to the experiment-

Table 1 Structural parameters (distances in Å, angles in °) of the strain-energy-minimized and the experimentally characterized co-ordinated and metal-free bispidine molecules [a]

	1^{b,c}	**2**^{b}	**3**^{b,d}	**4**^{e}	**5**^{c,e}	**6**^{c,e}	**7**^{c}	**9**^{c}
M−N(2)	2.16	2.09	2.12	2.14	2.15	2.19	2.139(6)	2.14
M−N(1)	2.17	2.14	2.12	2.18	2.19	2.25	2.134(6)	2.17
M−N(3)	2.11	2.09	2.09	2.11	2.12	2.12	2.085(9)	2.13
M−N(12)	2.11	2.09	2.09	2.11	2.12	2.12	2.093(9)	2.13
M−N(5)[O(7)]	2.18				2.15	2.20	2.281(6)	2.28
M−N(6)[O(8)]						2.18	2.067(6)	2.07
N(1)···N(2)^{f}	2.90	2.89	2.89	2.92	2.92	2.93	2.88	2.91
N(3)−M−N(12)	139	154	156	151	150	153	149.8(3)	150
N(1)−M−N(3)	110	102	104	96	97	94	94.0(3)	96
N(2)−M−N(3)	88	95	94	78	77	77	77.4(3)	77
N(1)−M−N(12)	110	102	94	96	97	94	99.3(3)	97
N(2)−M−N(12)	88	95	104	78	77	77	76.9(3)	77
N(1)−M−N(2)	84	86	86	85	85	83	84.8(2)	85
Strain energy/kJ mol^{-1}	74.9	67.5	65.4	56.1	57.3	59.7		57.4

[a] For structures and labelling, see Fig. 1 (L^2 and **7** are the experimental structures, Figs. 3 and 4, respectively; **9** is a computed structure with constrained nitrate geometry, see text). [b] Six-membered chelate rings involving the pyridine donors. [c] Angular geometries of the five- and six-co-ordinate species: N(5)[O(7)]−M−N(2) 174 (**1**), 164 (**5**), 96 (**6**), 116 (**7**) and 116 (**9**); N(5)[O(7)]−M−N(1) 101 (**1**), 110 (**5**), 180 (**6**), 159 (**7**) and 159 (**9**); N(5)[O(7)]−M−N(3) 90 (**1**), 100 (**5**), 85 (**6**), 89 (**7**) and 89 (**9**); N(6)[O(8)]−M−N(5)[O(7)] 84 (**6**), 59 (**7**) and 59 (**9**); N(6)[O(8)]−M−N(2) 180 (**6**), 174 (**7**) and 174 (**9**). [d] *trans*-Configuration. [e] Five-membered chelate rings involving the pyridine donors. [f] 2.92 Å for L^2.

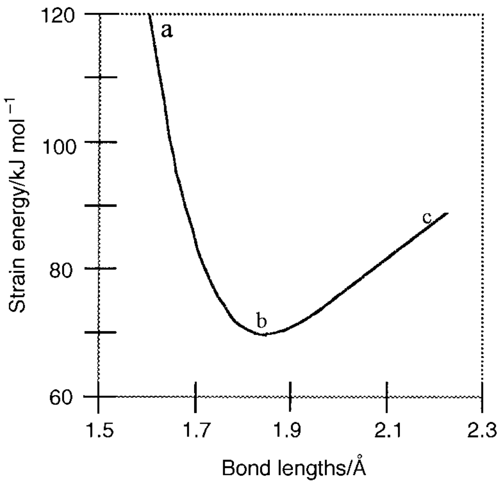
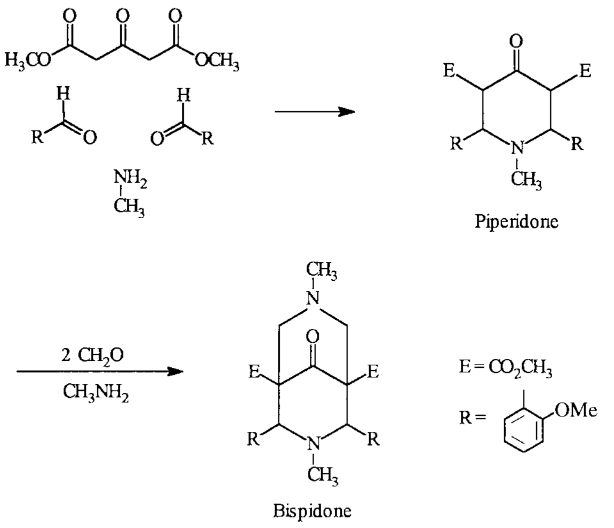


Fig. 2 Metal-donor-dependent strain energy of structure **2**. The plotted strain energies do not involve any metal-dependent terms (hole size of the free ligand). The four metal-donor distances have been varied independently[13] [plotted are the M−N(1) distances]. Parameters (Å, °, kJ mol^{-1}) for the extreme structures **a**, **b**, **c**: M−N(1) 1.58, 1.85, 2.14; M−N(2) 1.63, 1.86, 2.11; M−N(3) = M−N(12) 1.60, 1.85, 2.11; N(1)···N(2) 2.60, 2.84, 2.92; N(1)−M−N(2) 108, 100, 87; N(3)−M−N(12) 123, 135, 162; strain energy 120, 70, 82

ally determined co-ordinates, while the rest of the structure was optimized. These data are also included in Table 1 (structure **9**). (*ii*) Obviously, the parametrization of the potential-energy functions for the cobalt(II)-amine chromophore should be different for the three geometries studied here (four-, five- and six-co-ordinate), because any force field is ligand-field dependent.[12] However, the magnitude of this effect is not known, and not easy to quantify in the case of cobalt(II) amines. From the computation of the metal–donor-distance-dependent strain energy induced to the tetradentate ligand, in the case of the relevant tetrahedrally co-ordinated species (see discussion below), it emerges that the ligand is enforcing rather short metal–donor distances. This warrants the assumption that the metal–donor bonds are not considerably elongated in the tetrahedral geometry, where the effect due to a presumably somewhat longer strain-free distance might be balanced by a somewhat weaker stretching force constant.

From the computed structural data (Fig. 1, Table 1) it can be seen that the structure of the bispidine backbone is rather constant with a bite angle N(1)−M−N(2) of 85°, in excellent agreement with the data for the experimentally determined structure of the cobalt(II) compound. Also included in Table 1 is the experimentally determined structure of a metal-free bispidine derivative, and the N(1)···N(2) distances of all calculated and experimentally determined structures. These bite distances of the bispidine nitrogen atoms are approximately constant for all structures (2.88-2.93 Å). The bite angles involving the pyridine pendant arm are, as expected, dependent on the chelate ring size. For the ligand with the five-membered chelate ring, the N(2)−M−N(3) and N(2)−M−N(12) angles are constant and identical to the experimental data (77°). For the structures with the enlarged chelate rings these angles are larger and less constant (88 and 95°; the largest bite angle of 104° has been calculated for the complex of the ligand with *trans*- instead of *cis*-configurated substituents). This flexibility is due to the conformational freedom induced by the methyl group in the six-membered rings. In the five-co-ordinate compound with the larger chelate rings the van der Waals repulsion involving the extra ligand induces more puckering in these rings, and thus the smallest bite angles are observed in this series. Phenolate instead of methylpyridine substituents should lead to less flexibility in the six-membered chelate rings, and this idea will be pursued in our synthetic work. However, in our present modelling studies we decided to concentrate on a constant donor set. For the smaller chelate rings the angles involving the metal and the two pyridine groups are constant and identical to the experimental data (150°). Fig. 1 indicates that this leads to an open face opposite to the bispidine group, and it therefore was not unexpected that, experimentally, five- and six-co-ordinate species are observed. In the case of the larger chelate rings the bulky pyridyl groups are bent to the other side and partly shield the metal. The metal–ligand distances are rather constant over the whole series. The variation in angular geometry leads to some distortion, and an increase in co-ordination number to five or six is, due to ligand–ligand repulsion, generally accompanied by a small metal–donor elongation.

The rigidity of the bispidine type ligands is also demonstrated by the computed metal–donor-dependent strain energies for the ligand with a preference for distorted tetrahedral co-ordination geometry (structure **2**, see Fig. 2). The potential-energy curve has been obtained by constraining the metal–ligand distances, and the computed strain energies do not include any metal-dependent terms.[13,14] Thus, the curve is metal-ion independent and reflects the strain induced in the ligand by co-ordination to any metal ion. We note that the variation for the metal–amine and –pyridine donors is not expected to be identical (see also Table 1).[13] Hence, all four bonds have been varied independently, using the method described before.[13] Thus, the structures of complexes of the ligand with various metal ions [Co^{III}, Cr^{III}, Fe^{III} (low spin), Co^{II} and Cu^{II}] were calculated. The bond lengths M−N(1), M−N(2) and M−N(3) [M−N(12)] of these structures were then plotted against the ionic radius of the metal ion (average values for metal ions in similar complexes with amine and pyridine donors were used).[15] After choosing the appropriate start and end-points for all four bond lengths [1.868 and 2.087 for M−N(1), 1.862 and 2.048 for M−N(2) and 1.844 and 2.042 Å for M−N(3) and M−N(12)], the slopes of the plots allowed the determination of the step value for bond-length variation. Owing to the symmetry of the complex (C_s), the metal–pyridine bonds are equivalent while the metal–amine bonds are not (see also caption of Fig. 2). The rather steep potential-energy surface, with



Scheme 1 Bispidone synthesis

an optimum hole size of *ca.* 1.85 Å, supports the assumption of the bispidine-type ligand's rigidity and a preference for very short metal–donor distances.

The strain energies of all bispidine-type ligands, induced by co-ordination to cobalt(II), including four-, five- and six-co-ordinate species, obtained by co-ordination of extra ammonia or nitrate, are listed in Table 1. All metal-dependent energy terms are neglected, see above. Also, all interactions involving the extra ligands have been subtracted after the minimization process and before calculating the tabulated strain energies. Thus, the values listed in Table 1 are a measure of the strain induced by the metal ion and the extra ligands in the bispidine ligand, and they are quantitatively comparable within each series (five- or six-membered chelate rings of the pendant arms). It is arguable whether or not the van der Waals interactions involving the donor atoms (1,3-non-bonded interactions in the case of the ligand) should be subtracted or not. The energies tabulated include these values; a subtraction leads to 72.8, 66.5, 64.4, 49.4, 50.6, 53.6 kJ mol^{-1} for **1**, **2**, **3**, **5**, **6**, respectively, *i.e* not to any significant changes of the relative energies. It is evident that co-ordination of one or two extra ligands to a cobalt–bispidine fragment will generally increase the strain that the fragment induces in the bispidine ligand. This is borne out by the small increase in strain along the series of structures **4**–**6** (*ca.* 1 kJ mol^{-1} per extra ligand). This increase in strain will be overcompensated by the gain in bonding energy. From the tabulated strain energies it emerges that for the two ligands with the longer side chains (*cis* and *trans* configuration) a four-co-ordinate geometry is preferred by *ca.* 7 kJ mol^{-1}, while the energy differences for the ligand leading to smaller chelate rings are minimal. This suggests that in the latter case five- or six-co-ordinate compounds are obtained, and the bispidine's preference for either five- or six-co-ordination most likely depends on the size and type of the additional ligand. If this is large and bulky a trigonal-bipyramidal structure should be observed.

Preparative work

The synthesis of the two bispidones is described in Scheme 1. The piperidone predecessors of the bispidones L^1 and L^2 were synthesized in a Mannich Reaction of 2 mol of the pyridine-2-carbaldehyde or a correspondingly substituted benzaldehyde, and 1 mol each of the dimethyl ester of acetone dicarbonic acid [MeOC(O)CH$_2$C(O)CH$_2$C(O)OME] and methylamine, the main products being the *trans*-enoles. The latter isomerize in polar, protic solution and therefore react with 2 mol of formaldehyde and 1 mol of methylamine to form the bispidones.[16]

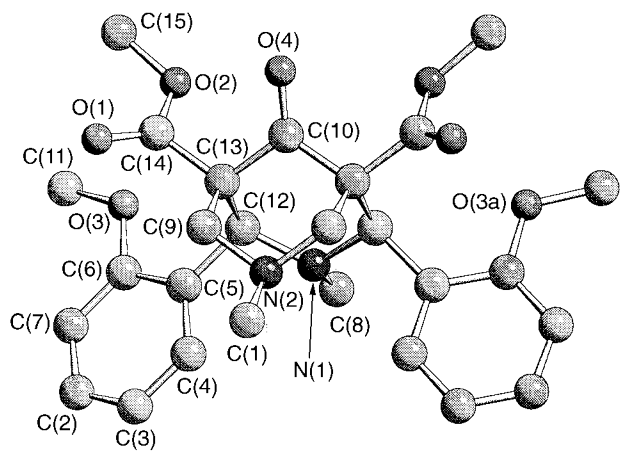


Fig. 3 The SCHAKAL[11] plot of the molecular structure of compound L^2

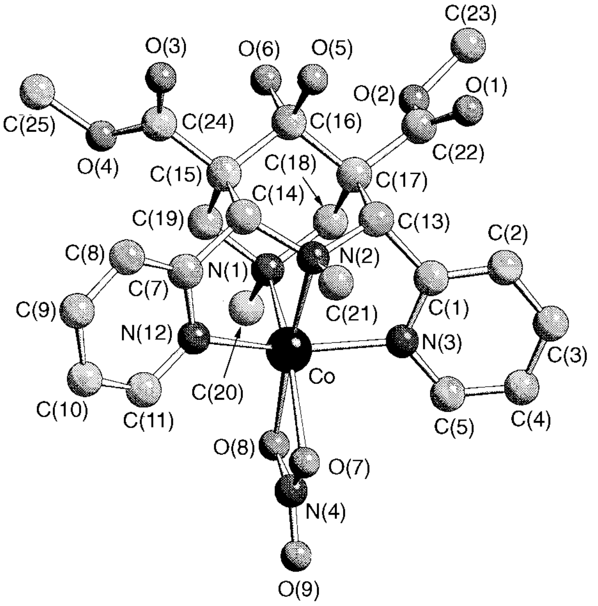


Fig. 4 The SCHAKAL[11] plot of the molecular structure of complex **7** as its nitrate monohydrate

Cobalt(II) complexes **7** and **8** were prepared from cobalt(II) nitrate or chloride, respectively. Addition of a solution of the cobalt salt in ethanol to a hot solution of ligand L^1 in ethanol and refluxing for 10–30 min produced the two complexes.[17] Crystals, suitable for X-ray diffraction, of the nitrate salt **7** were obtained by slow evaporation of the ethanolic solution. The structural analysis shows that, upon co-ordination to cobalt(II), the keto group has reacted to give an acetal. Since nitrate may co-ordinate as a bidentate ligand, based on the molecular modelling studies, this complex was assumed to exhibit a distorted-octahedral geometry. As discussed above, a larger monodentate ligand, such as chloride, should encourage a trigonal-bipyramidal geometry because it leaves little or no room for a sixth ligand, and the strain-energy difference between the bispidine in a trigonal-bipyramidal geometry and in an octahedral geometry is small (2.3 kJ mol^{-1}).

Experimentally determined structures

The SCHAKAL[11] plots of the experimentally determined structures of the bispidone L^2, and of the cobalt(II) compound **7** are presented in Figs. 3 and 4, respectively. The relevant structural parameters are compared to the computed data in Table 1. Both experimental structures show the expected chair–chair conformation of the bispidine backbone and the pendant arms in equatorial configurations. The overall structural features of the ligand backbone are very similar to each other and in excellent agreement with the predictions obtained by molecular mechanics calculations. In particular, the bite distance [N(1)···N(2), see Table 1] is almost identical for L^2 and the cobalt(II) compound **7**, supporting the predicted rigidity of these systems. The methoxy substituents of bispidone L^2 are, as expected, exposed to the periphery of the molecule, indicating that the only reorganization of this type of compound, required prior to co-ordination is, one rotation about each of two single bonds. The torsional barrier for a rotation around the C(13)– or C(14)–aromatic substituent axis has been found to be 70 kJ mol^{-1} for *m*-methyl-substituted aromatic systems.[16]

Experimental

Syntheses

The bispidones were prepared from the corresponding substituted piperidones.[16,18]

Compound L^1 was prepared as described in the literature.[16] Yield 80%, m.p. 181 °C (Found: C, 62.8; H, 6.1; N, 12.65. Calc. for $C_{23}H_{26}N_4O_5$: C, 63.05; H, 5.95; N, 12.8%). NMR ($CDCl_3$, 25 °C, $SiMe_4$): ^{1}H (200 MHz), δ 2.0 [s, 3 H, CHN(C*H*$_3$)CH], 2.25 [s, 3 H, CH_2N(C*H*$_3$)CH_2], 2.5 and 2.95 [2d, 4 H, ^2J(H–H) = 13.5 Hz, C*H*$_2$NCH$_3$], 3.85 (s, 6 H, OCH$_3$), 4.75 (s, 2 H, C*H*NCH$_3$) and 7.2-8.5 (4m, 8 H, aromatic H); ^{13}C (50 MHz), δ 43.20, 44.44 [N(CH$_3$)], 52.45 (OCH$_3$), 60.75 [*C*H$_2$N(CH$_3$)], 62.16 [*C*HN(CH$_3$)], 73.77 (*C*CO), 122.94-158.96 (aromatic C), 168.53 (CO) and 203.57 (CO). IR (KBr): $\tilde{\nu}$/cm^{-1} = 2968 (CH), 2850 (CH$_2$), 2811 (NCH$_3$), 1750 (C=O, ester), 1731 (C=O, keto group) and 1600 (pyridine H).

Compound L^2 was prepared by stirring a mixture containing the piperidone (8.83 g, 0.02 mol), aqueous formaldehyde solution (35%) (3.9 g, 0.048 mol) and aqueous methylamine (2.12 g, 0.024 mol) solution (37%) in acetone (40 cm^3) for 24 h at room temperature. After 2 d, the solid was collected by suction filtration and washed with cold ethanol. Yield 42%, m.p. 204 °C (Found: C, 65.05; H, 6.5; N, 5.55. Calc. for $C_{27}H_{32}N_2O_7$: C, 65.3; H, 6.45; N, 5.7%). NMR ($CDCl_3$, 25 °C, $SiMe_4$): ^{1}H (200 MHz), δ 1.78 [s, 3 H, CHN(C*H*$_3$)CH], 2.36 [s, 3 H, CH$_2$N(C*H*$_3$)CH$_2$], 2.4 and 3.4 [2 d, 4 H, ^2J(H–H) = 13.5 Hz, C*H*$_2$NCH$_3$], 3.71 (s, 6 H, OCH$_3$), 3.76 (s, 6 H, C$_6$H$_4$OC*H*$_3$), 5.0 (s, 2 H, C*H*NCH$_3$) and 6.8-8.2 (4 m, 8 H, H of Ph); ^{13}C (50 MHz), δ 42.23, 44.04 [N(CH$_3$)], 51.91 [*C*H$_2$N(CH$_3$)], 55.41 [*C*HN(CH$_3$)], 61.75 (*C*CO), 62.31 (OCH$_3$), 63.65 (OCH$_3$), 110.43–157.14 (aromatic C), 168.80 (CO), and 204.92 (CO). IR (KBr): $\tilde{\nu}$/cm^{-1} = 2890 (CH), 2870 (CH$_2$), 2792 (NCH$_3$), 1750 (C=O, ester) and 1740 (C=O, keto group).

Complex **7** was prepared as in ref. 17. Yield: 40%. Decomposition at 196 °C (Found: C, 42.5; H, 4.7; N, 12.7. Calc. for $C_{23}H_{26}CoN_6O_{12}\cdot 2H_2O$: C, 42.05; H, 4.55; N, 12.8%). IR (KBr): $\tilde{\nu}$/cm^{-1} = 2976 (CH), 2897 (CH$_2$), 1740 (C=O, ester), 1616 (pyridine H), 1391 (NO$_3^-$), 1267 (OH) and 1087 (C–O–H). Magnetic moment (field dependent) = 4.39 ± 0.01 μ_B, three unpaired electrons. UV/VIS (water): λ_{max} = 439, 489, 530 and 642 nm. A cyclic voltammogram displayed a quasi-reversible process, E_0 = 0.458 V (10^{-3} mol dm^{-3}) at a glassy carbon electrode in MeCN, scan rate 50 mV s^{-1}, Ag–AgNO$_3$ reference electrode, 0.1 mol dm^{-3} NBu$_4$ClO$_4$ in MeCN as supporting electrolyte.

Complex **8** was prepared by refluxing a 1 : 1 mixture of bispidone (250 mg) and CoCl$_2$ (71 mg) in absolute ethanol (15 cm^3) for 10 min. The product was isolated after adding diethyl ether to the solution. Yield 30%. Decomposition at 214 °C. IR (KBr): $\tilde{\nu}$/cm^{-1} = 2991 (CH), 2896 (CH$_2$), 1740 (C=O, ester), 1600 (pyridine H), 1267 (OH) and 1087 (C–O–H). Magnetic moment (field dependent) = 4.62 ± 0.02 μ_B, three unpaired electrons. UV/VIS (ethanol): λ_{max} = 512, 524, 551, 584 and 606 nm. A cyclic voltammogram showed an irreversible oxidation wave. The system is not as well defined as that of **7** and seems to decompose during oxidation; E_{ox} = 0.40 V (10^{-3} mol dm^{-3}), method as for **7**.

Crystallography

Compound L^2. $C_{27}H_{32}N_2O_7$, *M* = 496.56, colourless prisms (crystal dimensions 0.35 × 0.45 × 0.70 mm), orthorhombic, space group *Pnma* (no. 62), crystallographic mirror symmetry involving C(1), C(8), C(10) (see Fig. 3), a = 7.554(2), b = 22.98(1), c = 14.63(1) Å, U = 2540 Å^3, Z = 4, D_c = 1.30 cm^{-3}, F(000) = 1056, μ = 0.09 mm^{-1}, minimum, maximum transmission 0.95, 1.00.

3512 Reflections were measured under the same conditions as for complex **7**, and the structure was solved by direct methods. Full-matrix least-squares methods were used to refine 173 variables out of which 1512 reflections with $I > 2.5\sigma(I)$ converged at R = 0.069 and R' = 0.054; residual electron density 0.33, −0.27 e Å^{-3}. Weighting scheme $1/\sigma^2(F)$; goodness of fit = 2.37.

Complex 9·NO$_3$·H$_2$O. $C_{23}H_{28}CoN_6O_{13}$, *M* = 655.44, brown plates (crystal dimensions 0.15 × 0.25 × 0.35 mm), triclinic, space group $P\bar{1}$ (no. 2), a = 10.79(1), b = 11.35(1), c = 12.84(2) Å, α = 70.18(9), β = 82.09(9), γ = 66.69(8)°, U = 1359 Å^3, Z = 2, D_c = 1.60 g cm^{-3}, F(000) = 678, μ = 0.70 mm^{-1}, minimum, maximum transmission 0.87, 1.00.

5509 Reflections were measured at room temperature on a Nicolet R3-diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å); ω scan mode, data reduction and application of Lorentz-polarization and absorption corrections (empirical) were carried out. The structure was solved by Patterson–Fourier methods with the SHELXTL PLUS program;[19] hydrogen atoms were included at calculated sites with fixed isotropic thermal parameters. The refinement (full-matrix, least-squares methods, $|F|$) of 388 variables out of 6037 reflections with $I > 2.5\sigma(I)$ converged at R = 0.084 and R' = 0.063; residual electron density 0.76 and −0.63 e Å^{-3}. Weighting scheme $1/\sigma^2(F)$; goodness of fit = 1.89.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/308.

Measurements and calculations

The computer program MOMEC[8] with a published parameter set[9] was used for molecular mechanics calculations. Proton and ^{13}C NMR spectra at 200 and 50.32 MHz were obtained with a Bruker AS 200 instrument with 3-trimethylsilylpropionate as an internal reference. Infrared spectra (KBr pellets) were measured with a Perkin-Elmer 16PC FT-IR instrument, UV/VIS spectra with a Varian Cary IE spectrophotometer. Magnetic measurements were recorded on a Bruker Faraday balance at 25 °C. Electrochemical measurements were made with a BAS 100B system using 1 × 10^{-3} mol dm^{-3} solutions of the metal complexes in acetonitrile at a glassy carbon electrode with a Ag–AgNO$_3$ reference electrode. Elemental analyses were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg.

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