Stereochemistry of Six-co-ordinate Bis(tridentate ligand)metal Complexes

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Repulsion-energy calculations show that the *mer* isomer of [M(tridentate ligand)$_2$] exists as a potential-energy minimum at all values of the normalised bite, *b*, of the chelate rings, whereas the two *fac* isomers exist only at high values of the normalised bite. The *mer* isomer is generally more stable than the *fac* isomers. The *unsym-fac* isomer formed with ligands of small normalised bite is not closely related to the octahedron, but approaches a skew rectangular bipyramid, or trigonal prism, the latter description being particularly appropriate for unsymmetrical tridentate ligands. These predictions are compared with known crystal structures.

THE stereochemistry of complexes containing polydentate ligands is often considerably distorted compared with complexes containing only unidentate ligands. Previous work with six-co-ordinate complexes containing bi- and/or uni-dentate ligands has shown that the stereochemistry can be very well predicted from a consideration of the repulsion between valence-shell electron pairs and/or ligand donor atoms.[1-3] This approach is now extended to complexes containing two tridentate ligands.[3-5]

METHOD

The donor atoms of two equivalent tridentate ligands are labelled ABC and DEF respectively. If the ligand is symmetrical, that is, the AB arm is the same as the BC arm, the normalised bite is given by $b = AB/r = BC/r$, where r is the metal–ligand distance. For unsymmetrical tridentate ligands the two arms of the ligand are not equal, and the two different normalised bites are defined such that $b_1 > b_2$. The tridentate ligands are assumed to be freely hinged at the central donor atoms B and E respectively, and the repulsions between the end donor atoms, A and C, and D and F, are included in the total-energy expression. Only single-chain tridentate ligands are considered, and ligands with more complex branching, such as ' tripods,' are exluded.

The repulsion-energy coefficients, X, which are a direct measure of the stability of the particular stereochemistry,

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[1] D. L. Kepert, *Progr. Inorg. Chem.*, 1977, **23**, 1.

[2] D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561; 1973, **12**, 1944; *J. Organometallic Chem.*, 1976, **107**, 49.

[3] M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, *J.C.S. Dalton*, 1977, 1350.

[4] D. L. Kepert, *J.C.S. Dalton*, 1974, 612.

[5] D. L. Kepert, A. H. White, and A. C. Willis, *J.C.S. Dalton*, 1977, 1342.

were calculated as before,[1-5] the minimum on the potential-energy surfaces being located to 0.1° in each of the angular co-ordinates. The previous custom of using values of 1, 6, and 12 for n in the repulsion-energy function was continued. No symmetry elements were assumed in the calculations.

RESULTS

Three isomers were obtained as potential-energy minima, which for $b = 2^{\frac{1}{2}}$ are the usual *meridional, symmetrical-facial-*, and *unsymmetrical-facial* octahedral isomers (Figure 1). The *mer* isomer contains a two-fold axis through BME, and exists as a potential-energy minimum at all values of the normalised bite. For symmetrical tridentate ligands the two ligands are coplanar with the metal atom, and perpendicular to each other, the symmetry being C_{2v}. For unsymmetrical ligands the dihedral angle between the two shorter arms becomes slightly less than 90°.

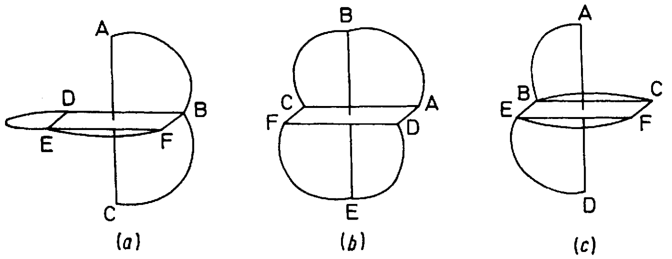

FIGURE 1 Isomers for [M(tridentate ligand)$_2$]: (*a*) *mer*, (*b*) *sym-fac*, and (*c*) *unsym-fac*

For symmetrical tridentate ligands the *sym-fac* isomer exists as a potential-energy minimum only at relatively large values of the normalised bite ($n = 1$, $b \geqslant 1.08$; $n = 6$, $b \geqslant 1.10$; $n = 12$, $b \geqslant 1.12$). This isomer contains a mirror plane, an inversion centre, and a two-fold axis, with C_{2h} symmetry. In addition, the calculations show that ACFD remains a perfect square at all times. Two isomers can be produced by introducing two unsymmetrical ligands. The first, *sym-fac*-(1), has AB and DE as the short arms and retains the two-fold axis. As the difference between b_1 and b_2 is increased the angle between the ABD and ADE octahedral faces decreases, but an ABDE plane is never attained. The second isomer, *sym-fac*-(2), has AB and EF as the short arms and retains the centre of inversion at the metal atom. The ACDF atoms remain as a square.

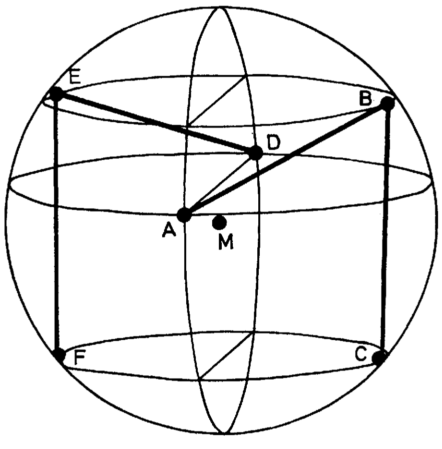

FIGURE 2 *unsym-fac*-[M(tridentate ligand)$_2$]

The most interesting result from these calculations concerns the *unsym-fac* isomer, which also exists as a potential-energy minimum only at relatively large normalised bites ($n = 1$, $b \geqslant 1.16$; $n = 6$, $b \geqslant 1.12$; $n = 12$, $b \geqslant 1.08$). The angular co-ordinates are defined with respect to Figure 2. The ϕ_i co-ordinates are defined as the angle between the M–i bond and the two-fold axis bisecting BE, AD, and CF. The θ_i co-ordinates are defined relative to $\theta_A = 0$ and $\theta_D = 180°$. The variation of these angular co-ordinates with normalised bite is shown in Figure 3, calculated for $n = 6$. Similar results are obtained for $n = 1$ and 12. The major point of interest is that ϕ_A approaches ϕ_B at low values of the normalised bite, so that ABDE approaches a rectangle. At the same time, θ_C increases as θ_B decreases. The resulting stereochemistry, viewed normal to this ABDE plane, is shown in Figure 4(*b*). This stereochemistry is not closely related to the regular octahedron, but could be considered as being intermediate between a trigonal prism [$\theta_C = 90° + (\theta_B/2)$] [Figure 4(*a*)] and a skew rectangular bipyramid with A and D as the apical sites ($\theta_C = \theta_B$) [Figure 4(*c*)]. Another feature of this stereochemistry is that different individual atom-repulsion energies [1] are associated with the two ends of the tridentate ligand (Figure 5). For normalised bites less than $2^{\frac{1}{2}}$ atom A experiences greater repulsion than does C, whereas the reverse is true for $b > 2^{\frac{1}{2}}$. Three isomers can

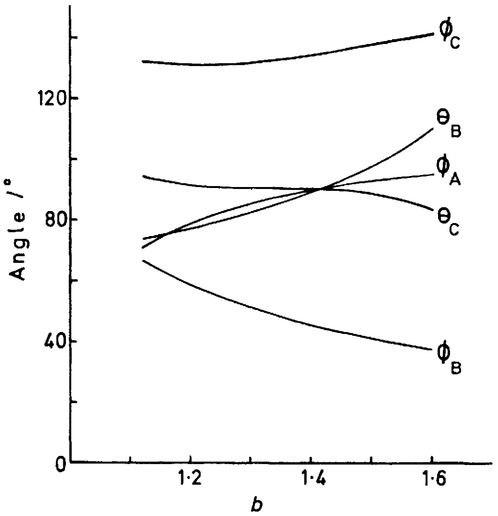

FIGURE 3 Angular co-ordinates for *unsym-fac*-[M(tridentate ligand)$_2$] as a function of normalised bite b; $n = 6$

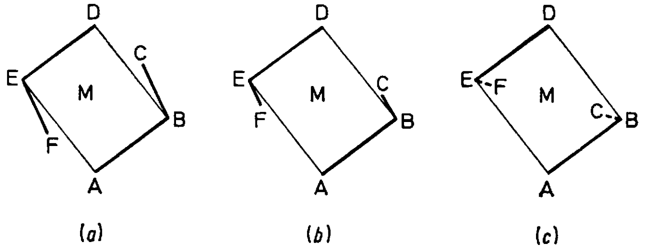

FIGURE 4 *unsym-fac*-[M(tridentate ligand)$_2$]: (*a*) trigonal prism, (*b*) intermediate, (*c*) skew rectangular bipyramid be produced by introducing unsymmetrical ligands. The first, *unsym-fac*(1), retains the two-fold axis and has AB and DE as the short arms and BC and EF as the long arms. As would be expected from an examination of Figure 4, this leads to a decrease in θ_B with further distortion towards a trigonal prism [Figure 4(*a*)]. The second isomer, *unsym-fac*-(2), also retains the two-fold axis, has BC and EF as the short arms, and decreases the distortion towards $\phi_A = \phi_B$ which leads to the unusual stereochemistry described above. The third isomer, *unsym-fac*(3), retains no symmetry elements but is generally similar to *unsym-fac*-(1) and -(2).

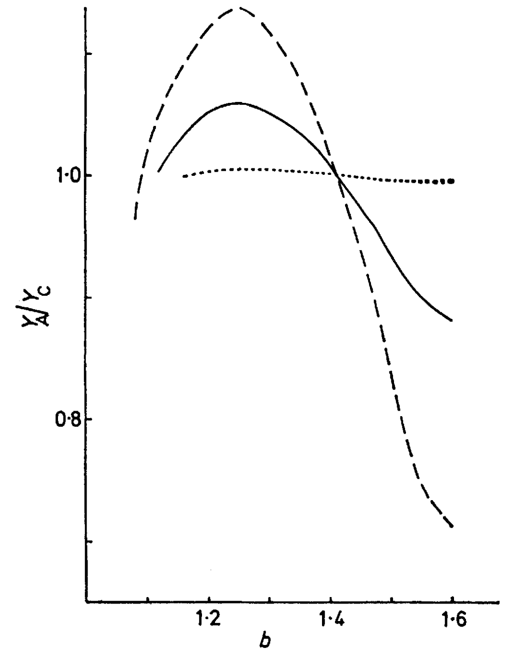

FIGURE 5 Ratio of the individual atom-repulsion coefficients for the two ends of each tridentate ligand in *unsym-fac*-[M(tridentate ligand)$_2$], as a function of normalised bite *b*: $n = 1$ (· · · ·), 6 (——), or 12 (– – – –)

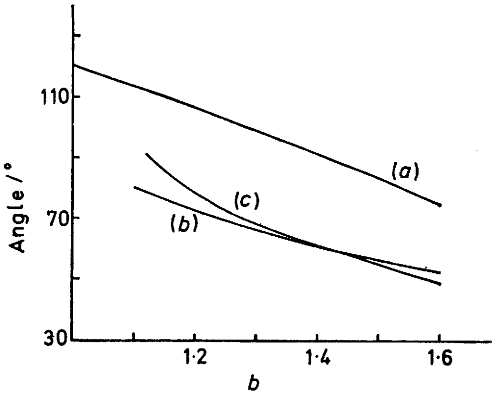

FIGURE 6 Tridentate angle as a function of normalised bite *b* ($n = 6$) for the *mer* (*a*), *sym-fac* (*b*), and *unsym-fac* isomer (*c*)

One angular parameter of importance when comparing different isomers is the tridentate angle ABC (Figure 6), which is in the order *mer* $\gg$ *unsym-fac* $>$ *sym-fac* for $b < 2^{\frac{1}{2}}$.

DISCUSSION

The two *fac*-isomers only exist as discrete potential-energy minima above a normalised bite of *ca.* 1.1, whereas the *mer*-isomer exists as a minimum at all values of the normalised bite. The stability of the *fac* isomers relative to the *mer* isomer is shown in Figure 7, calculated for $n = 6$. Similar results are obtained for $n = 1$ and 12. It is predicted that the *mer* isomer is significantly stabilised below $b \sim 1.3$ the *unsym-fac* isomer above $b \sim 1.5$, all three isomers being possible between these limits. Similar results are obtained for unsymmetrical tridentate ligands, typical values being shown in Figure 8. It can be seen that *sym-fac*-(2) is less stable than *sym-fac*-(1), and *unsym-fac*-(2) is less stable than *unsym-fac*-(1) and -(3).

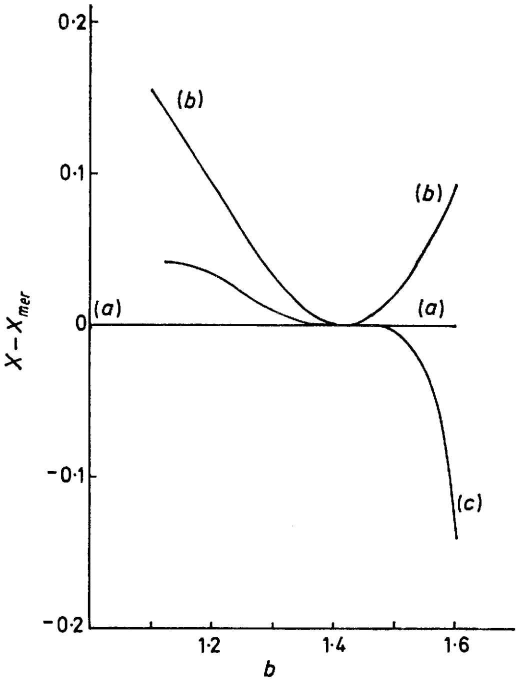

FIGURE 7 Relative repulsion-energy coefficients for [M(tridentate ligand)$_2$] as a function of normalised bite *b* ($n = 6$). Isomers as in Figure 6

These predictions are in agreement with the crystal structures determined for the isomers (Table 1). There is only one example of a *fac*-isomer with $b < 1.3$, compared with 10 *mer* isomers. The predicted order of isomer stability is also in agreement with the observed equilibrium mixture of $[Co\{NH(CH_2CH_2NH_2)_2\}_2]^{3+}$ isomers in water, dimethyl sulphoxide, and dimethylacetamide, of *ca.* 10(*mer*) : 3(*unsym-fac*) : 1(*sym-fac*).[6] This implies that one unit in the repulsion-energy coefficient for six-co-ordination is *ca.* 600 kJ mol^{-1} (for $n = 6$), in accord with previous estimates.[1] A similar study[7] using $S(CH_2CH_2NH_2)_2$ as the tridentate ligand showed only the existence of the *fac* isomers. However, such

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[6] F. R. Keene and G. H. Searle, *Inorg. Chem.*, 1974, **13**, 2173.

[7] G. H. Searle and E. Larsen, *Acta Chem. Scand.*, 1976, **A30**, 143.

ligands with large donor atoms at the hinging B site, and which form five-membered chelate rings with the metal atom, cannot behave as tridentate ligands with large values of the tridentate angle ABC, as is required for the *mer* isomer (Figure 6).[3,4]

TABLE 1

Stereochemistry of bis(tridentate) complexes [a]

Complex	b_1	b_2	ABC/°	Stereochemistry
$Na[Co(salgly)_2]\cdot 3H_2O$ [b]	1.49	1.36	89	*mer*
$[Co(OH_2)_6][Co(salgly)_2]_2\cdot 2H_2O$ [c]	1.48	1.36	89	*mer*
$[Co(asal)_2]I\cdot H_2O$ [d]	1.47	1.35	90	*mer*
$[Cr(asal)_2]I$ [e]	1.43	1.31	94	*mer*
$[Ni\{NH(CH_2CH_2CH_2NH_2)_2\}_2][ClO_4]_2$ [f]	1.43		89	*mer*
$[Co\{NH(CH_2CH_2NH_2)_2\}_2]Br_3$ [g]	1.38		62	*sym-fac*
$K_2[Cu\{NH(CH_2CO_2)_2\}_2]\cdot H_2O$ [h]	1.37	1.23	63	*sym-fac*
$K[Co\{NH(CH_2CO_2)_2\}_2]\cdot 2.5H_2O$ [i]	1.37		64	*unsym-fac*
$[Co\{NH(CH_2CH_2NH_2)_2\}_2][Co(CN)_6]\cdot 2H_2O$ [j]	1.36		64	*unsym-fac*
$[Co\{NH(CH_2CH_2NH_2)_2\}_2][NO_3]_3\cdot H_2O$ [k]	1.36		95	*mer*
$[Cu\{NH(CH_2CONH_2)_2\}_2][ClO_4]_2$ [l]	1.36	1.17	68	*sym-fac*
$[Cu(NH_2CH_2CH_2NHCH_2CH_2OH)_2][ClO_4]_2$ [m]	1.35	1.23	76	*unsym-fac*
$K_4[Ni\{N(CH_2CO_2)_3\}_2]\cdot 8H_2O$ [n]	1.36	1.25	63	*sym-fac*
$K_2[Ni\{S(CH_2CO_2)_2\}_2]\cdot 3H_2O$ [o]	1.35		63	*unsym-fac*
$[Co(tan)_2](Cl,I)\cdot 2CHCl_3$ [p]	1.34	1.31	97	*mer*
$[V(aabh)_2]$ [q]	1.33	1.22		*unsym-fac*
$[Ni(dapd)_2]$ [r]	1.32		98	*mer*
$Li_2[Ni\{NH(CH_2CO_2)_2\}_2]\cdot 4H_2O$ [s]	1.32		64	*sym-fac*
$Cs_2[Ni\{NH(CH_2CO_2)_2\}_2]\cdot 4H_2O$ [s]	1.31		65	*sym-fac*
$[Ni\{N(CH_2CH_2OH)_3\}_2][NO_3]_2$ [t]	1.31		67	*sym-fac*
$[Ni\{NH(CH_2CONH_2)_2\}_2][ClO_4]_2$ [u]	1.31		68	*unsym-fac*
$[Ni\{NH(CH_2CH_2NH_2)_2\}_2]Cl_2\cdot H_2O$ [v]	1.31		98	*mer*
$[Cu\{NH(CH_2CH_2NH_2)_2\}_2][NO_3]_2$ [w]	1.30		98	*mer*
$[Cu\{NH(CH_2CH_2NH_2)_2\}_2]Br_2\cdot H_2O$ [x]	1.29		99	*mer*
$[Zn\{NH(CH_2CH_2NH_2)_2\}_2][NO_3]_2$ [y]	1.28		100	*mer*
$[Co(meto)_2]$ [z]	1.28	1.15	104	*mer*
$[Co(terpy)_2][SCN]_2$ *	1.28		101	*mer*
$[Co(terpy)_2]Br_2\cdot 3H_2O$ †	1.27		101	*mer*
$[Ni\{NH(CH_2CNH_2NOH)_2\}_2]Cl\cdot 2H_2O$ ‡	1.27		66	*sym-fac*
$[Ni(Hpydca)_2]\cdot 3H_2O$ §	1.26		102	*mer*
$[Zn(purp)_2]\cdot 4H_2O$ ¶	1.25		103	*mer*
$[Cu(purp)_2]\cdot 5H_2O$ ¶	1.24		103	*mer*
$H_2[Ag(pydca)_2]\cdot H_2O$ ‖	1.21		106	*mer*

[a] salgly = Salicylideneglycinate; asal = *N*-2-aminoethylsalicylaldiminate; tan = 1-(2-thiazolylazo)-2-naphtholate; aabh = acetylacetone benzoylhydrazonate; dapd = 2,6-diacetylpyridine dioximate; meto = 3-*o*-chlorophenyl-1-methyltriazene-1-oxide; terpy = 2,2′:6′,2″-terpyridyl; pydca = pyridine-2,6-dicarboxylate; purp = purpurate. [b] G. G. Aleksandrov, Y. T. Struchkov, and Y. N. Belokon, *J. Struct. Chem.*, 1975, **16**, 805. [c] L. R. Nassimbeni, G. C. Percy, and A. L. Rodgers, *Acta Cryst.*, 1976, **B32**, 1252. [d] T. H. Benson, M. S. Bilton, and N. S. Gill, *Austral. J. Chem.*, 1977, **30**, 261. [e] A. P. Gardner, B. M. Gatehouse, and J. C. B. White, *Acta Cryst.*, 1971, **B27**, 1505. [f] S. Biagini and M. Cannas, *J. Chem. Soc.* (*A*), 1970, 2398. [g] M. Kobayashi, F. Marumo, and Y. Saito, *Acta Cryst.*, 1972, **B28**, 470. [h] F. G. Karamenko, T. N. Polynova, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1973, **14**, 1043. [i] A. B. Corradi, C. G. Palmieri, M. Nardelli, M. A. Pellinghelli, and M. E. V. Tani, *J.C.S. Dalton*, 1973, 655. [j] M. Kono, F. Marumo, and Y. Saito, *Acta Cryst.*, 1973, **B29**, 739. [k] E. D. Sancilio, L. F. Druding, and D. M. Lukaszewski, *Inorg. Chem.*, 1976, **15**, 1626. [l] M. Sekizaki, *Bull. Chem. Soc. Japan*, 1974, **47**, 1447. [m] R. V. Chastain and T. L. Dominick, *Inorg. Chem.*, 1973, **12**, 2621. [n] V. V. Fomenko, T. N. Polynova, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1975, **16**, 602. [o] J. Delaunay, C. Kappenstein, and R. Hugel, *Acta Cryst.*, 1976, **B32**, 2341. [p] M. Kurahashi, *Acta Cryst.*, 1976, **B32**, 1611. [q] Ref. 8. [r] G. Sproul and G. D. Stucky, *Inorg. Chem.*, 1973, **12**, 2898. [s] N. J. Mammano, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1977, **B33**, 1251. [t] K. Nielson, R. G, Hazell, and S. E. Rasmussen, *Acta Chem. Scand.*, 1972, **26**, 889. [u] M. Sekizaki, *Acta Cryst.*, 1976, **B32**, 1568. [v] S. Biagini and M. Cannas, *J. Chem. Soc.* (*A*), 1970, 2398. [w] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 883. [x] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 2233. [y] M. Zocchi, A. Albinati, and G. Tieghi, *Cryst. Struct. Comm.*, 1972, **1**, 135. [z] G. L. Dwivedi and R. C. Srivastava, *Acta Cryst.*, 1971, **B27**, 2316. * C. L. Raston and A. H. White, *J.C.S. Dalton*, 1976, 7. † E. N. Maslen, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1974, 1803. ‡ D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1865. § P. Quaglieri, H. Loiseleur, and G. Thomas, *Acta Cryst.*, 1972, **B28**, 2583; H. Gaw, W. R. Robinson, and R. A. Walton, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 695; A. Chiesi Villa, C. Guastini, A. Musatti, and M. Nardelli, *Gazzetta*, 1972, **102**, 226. ¶ A. H. White and A. C. Willis, *J.C.S. Dalton*, 1977, 1372. ‖ The hydrogen atoms were not located. Both ligands are symmetrical, but different, $b = 1.24$ and 1.17 [M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1970, 1405].

With the exception of the *fac* isomers of the copper(II) complexes which are tetragonally distorted due to two copper–oxygen bonds being *ca.* 25% longer than the other two, and the nickel complex with nitrilotriacetate, there is good agreement between the calculated and observed structures.

In agreement with predictions, the four end donor atoms of the two tridentate ligands describe a reasonable square in the *sym-fac* isomers, the distortions from the regular octahedron resulting from a decrease in normalised bite being accommodated by bond angles involving the hinging B and E atoms (Table 2).

The detailed structural parameters of complexes with

TABLE 2

Bond angles (°) in *sym-fac*-[M(tridentate ligand)$_2$]

Complex	AMC	AMD	AMB	AME
$[Co\{NH(CH_2CH_2NH_2)_2\}_2]Br_3$	90	90	87	93
$Li_2[Ni\{NH(CH_2CO_2)_2\}_2]\cdot 4H_2O$	89	91	83	97
$Cs_2[Ni\{NH(CH_2CO_2)_2\}_2]\cdot 4H_2O$	90	90	82	98
$[Ni\{N(CH_2CH_2OH)_3\}_2][NO_3]_2$	92	88	82	98
$[Ni\{NH(CH_2CNH_2NOH)_2\}_2]Cl\cdot 2H_2O$	88	92	79	101

the *unsym-fac* stereochemistry, containing two symmetrical tridentate ligands, are listed in Table 3. These parameters are in good agreement with the predicted distortions from the regular octahedron (Figure 3).

TABLE 3

Structural parameters of *unsym-fac*-[M(tridentate ligand)$_2$]

Complex	b	MA/MC	Angle/° ϕ_A	ϕ_B	θ_B	ϕ_C	θ_C
$K[Co\{NH(CH_2CO_2)_2\}_2]\cdot 2.5H_2O$	1.37	0.99	90	49	87	135	93
$[Co\{NH(CH_2CH_2NH_2)_2\}_2][Co(CN)_6]\cdot 2H_2O$	1.36	1.01	88	48	86	134	91
$K_2[Ni\{S(CH_2CO_2)_2\}_2]\cdot 3H_2O$	1.35	1.01	91	51	83	135	90
$[Ni\{NH(CH_2CONH_2)_2\}_2][ClO_4]_2$	1.31	1.02	85	54	83	136	91

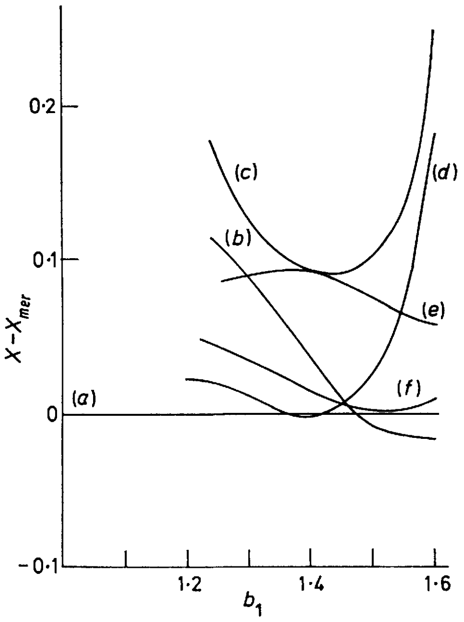

FIGURE 8 Relative repulsion-energy coefficients for [M(unsymmetrical tridentate ligand)$_2$] as a function of normalised bite b_1 (b_2/b_1 = 0.8, n = 6) for the *mer* (*a*), *sym-fac* (1) (*b*), *sym-fac* (2) (*c*), *unsym-fac* (1) (*d*), *unsym-fac* (2) (*e*), and *unsym-fac* (3) (*f*) isomers

As the normalised bite is decreased from $2^{\frac{1}{2}}$ to *ca.* 1.3, the difference ($\phi_A - \phi_B$) decreases from 45 to *ca.* 35°, and the difference ($\theta_C - \theta_B$) increased from 0 to *ca.* 10°. The M–A bond simultaneously becomes slightly longer than the M–B bond, also as predicted (Figure 5).

The results above show that the *unsym-fac*-(1) isomer is stabilised if unsymmetrical tridentate ligands are used, and that this isomer is closely related to the trigonal prism. It is significant that in a preliminary report[8] of [V(aabh)$_2$], the structure was described as trigonal prismatic (aabh is the dianion of acetylacetone benzoylhydrazone, $[PhCONNCMeCHCOMe]^{2-}$). There is approximate two-fold symmetry, the two-fold axis being normal to the rectangular face formed by the two five-membered chelate rings, with the other two donor atoms being connected through six-membered chelate rings (b_1 1.33, b_2 1.22). This general type of ligand design may be a convenient way of stabilising complexes with approximate trigonal-prismatic stereochemistry, particularly if the *mer* isomer is destabilised by using large hinging atoms. The only other *unsym-fac* isomer containing unsymmetrical tridentate ligands is $[Cu(NH_2CH_2CH_2NHCH_2CH_2OH)_2][ClO_4]_2$, which is tetragonally elongated [Cu–2(O) 2.47, Cu–4(N) 2.03Å, b_1 1.35, and b_2 1.23].

It is important to note that the tridentate angles ABC are in very good agreement with those predicted (Table 1 and Figure 6). This is observed even for the same ligand, for example, $NH_2CH_2CH_2NHCH_2CH_2NH_2$, in different six-co-ordinate isomers or even in five-co-ordinate complexes,[4] confirming the assumption made above that these single-chain ligands may be considered as freely hinged.

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[8] A. A. Diamantis, M. R. Snow, and J. A. Vanzo, *J.C.S. Chem. Comm.*, 1976, 264.