Crystal Structure of Bis(isocyanato)(2,2′:6′,2″-terpyridyl)cobalt(II): Stereochemistry of [M(tridentate ligand)(unidentate ligand)$_2$] Complexes

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The title compound, [Co(terpy)(NCO)$_2$], has been synthesized and its crystal structure determined by single-crystal *X*-ray diffraction methods, being refined to a residual of 0.048 for 715 ' observed ' reflections. Crystals are monoclinic, space group *C*2/*c*, with *a* = 16.351(6), *b* = 9.202(3), *c* = 13.048(4) Å, β = 124.70(3), and *Z* = 4. The molecule containing five-co-ordinate cobalt(II) has internal crystallographically imposed *2* symmetry: Co–N (terpy) 1.949(4), 2.146(7); Co–N(NCO) 2.058(6) Å. The co-ordination geometry about the metal atom is examined in terms of a repulsion model.

MANY bivalent transition-metal species form complexes of the type [MLX$_2$] where L is 2,2′:6′,2″-terpyridyl (terpy) and X is a negatively charged unidentate ligand.[1-4] Structural data are available for [Co(terpy)Cl$_2$],[5] [Zn(terpy)Cl$_2$],[6] and [Cd(terpy){Mn(CO)$_5$}$_2$],[7] showing the metal atom to be five-co-ordinate. In [Co(terpy)(OH)(CO$_3$)],[8] by contrast, six-co-ordination is preferred in spite of the smaller metal radius. In order to ascertain the variation in metal stereochemistry in complexes of the type [MLX$_2$] when the effective size of the unidentate ligand is changed, it was decided to determine the structure of [Co(terpy)(NCO)$_2$] for comparison; the complex was prepared by reaction of stoicheiometric proportions of terpy and cobalt(II) cyanate.

EXPERIMENTAL

Crystal Data.—$C_{17}H_{11}CoN_5O_2$, $M = 376.2$, Monoclinic, space group *C*2/*c* (C^6_{2h}, no. 15), $a = 16.351(6)$, $b = 9.202(3)$, $c = 13.048(4)$ Å, $\beta = 124.70(3)°$, $U = 1\,614(2)$ Å^3, $D_m = 1.53(1)$, $Z = 4$, $D_c = 1.54$ g cm^{-3}, $F(000) = 764$, nickel-filtered Cu radiation, $\lambda = 1.541\,8$ Å, $\mu = 84.1$ cm^{-1}, crystal size 0.18 × 0.15 × 0.73 mm (prism), $T = 295(1)$ K.

TABLE 1

Atomic fractional cell co-ordinates

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Co	0.000 0(—)	0.302 7(1)	0.250 0(—)
N(1)	0.000 0(—)	0.526 3(7)	0.250 0(—)
C(1A)	0.050 0(4)	0.594 4(7)	0.210 0(5)
C(2A)	0.049 6(6)	0.748 3(9)	0.210 3(7)
H(2A)	0.083(5)	0.782(8)	0.174(6)
C(3)	0.000 0(—)	0.819 2(14)	0.250 0(—)
H(3)	0.000(—)	0.926(11)	0.250(—)
N(2A)	0.085 1(3)	0.358 3(6)	0.177 2(4)
C(4A)	0.097 9(5)	0.501 4(8)	0.167 3(5)
C(5A)	0.127 1(5)	0.264 6(9)	0.139 5(6)
H(5A)	0.110(3)	0.148(6)	0.142(4)
C(6A)	0.152 1(7)	0.550 0(12)	0.121 5(8)
H(6A)	0.153(5)	0.658(8)	0.120(6)
C(7A)	0.180 2(5)	0.307 0(13)	0.092 8(7)
H(7A)	0.208(5)	0.229(8)	0.059(7)
C(8A)	0.192 1(7)	0.452 0(15)	0.084 0(8)
H(8A)	0.225(7)	0.464(11)	0.045(9)
N(2)	0.098 9(4)	0.182 2(5)	0.389 2(5)
C(2)	0.138 4(5)	0.118 6(7)	0.478 8(7)
O(2)	0.182 7(5)	0.051 6(6)	0.574 5(5)

TABLE 2

Molecular geometry (non-hydrogen atoms)

Distances (Å)

Co–N(1)	2.058(6)	C(2A)–C(3A)	1.353(13)
Co–N(2A)	2.146(7)	C(4A)–N(2A)	1.351(9)
Co–N(2)	1.949(4)	C(4A)–C(6A)	1.395(16)
N(2)–C(2)	1.126(9)	N(2A)–C(5A)	1.357(11)
C(2)–O(2)	1.197(9)	C(5A)–C(7A)	1.372(15)
N(1)–C(1A)	1.349(9)	C(7A)–C(8A)	1.362(18)
C(1A)–C(4A)	1.467(12)	C(8A)–C(6A)	1.359(18)
C(1A)–C(2A)	1.416(10)		

Angles (°)

N(2)–Co–N(2)	110.6(2)
N(2)–Co–N(2A)	98.4(3)
N(2)–Co–N(2B)	97.2(3)
N(2)–Co–N(1)	124.7(1)
N(1)–Co–N(2A)	76.2(1)
N(2A)–Co–N(2B)	152.4(2)
Co–N(2)–C(2)	160.9(8)
N(2)–C(2)–O(2)	178.3(11)
Co–N(1)–C(1A)	117.7(4)
Co–N(2A)–C(4A)	116.7(5)
Co–N(2A)–C(5A)	126.8(5)
C(1A)–N(1)–C(1B)	124.6(6)
C(4A)–N(2A)–C(5A)	116.6(7)
N(1)–C(1A)–C(4A)	116.6(6)
C(4A)–C(1A)–C(2A)	126.1(8)
N(1)–C(1A)–C(2A)	117.3(8)
C(1A)–C(2A)–C(3A)	119.2(10)
C(2A)–C(3A)–C(2B)	122.3(11)
C(1A)–C(4A)–N(2A)	112.8(7)
C(1A)–C(4A)–C(6A)	125.6(7)
N(2A)–C(4A)–C(6A)	121.6(8)
C(4A)–C(6A)–C(8A)	119.7(10)
C(6A)–C(8A)–C(7A)	119.9(12)
C(8A)–C(7A)–C(5A)	118.2(11)
C(7A)–C(5A)–N(2A)	124.0(8)

Structure Determination.—A unique data set was measured within the limit $2\theta_{max.}$ 100° using a Syntex $P\bar{1}$ four-circle diffractometer in conventional 2θ—θ scan mode, yielding 836 independent reflections, 715 with $I > 2\sigma(I)$ being considered ' observed ' and used in the full-matrix least-squares refinement after analytical absorption correction and solution by direct methods. Positional parameters of all atoms were refined; thermal parameters were refined isotropically for hydrogen atoms and anisotropically for the remainder. Final residuals were *R* 0.048 and *R*′ 0.054, reflection weights being $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral-atom scattering factors were used throughout, those for Co being corrected for anomalous dispersion (f', f'').[9-11] Calculations were made using the ' *X*-RAY '76 ' program system [12] on a CYBER 73 computer. Final atomic co-ordinates are in Table 1, bond distances and angles in Table 2. The hydrogen-atom geometries, least-squares planes, thermal parameters, and structure factor amplitudes have been deposited as Supplementary Publication No. SUP 22797 (7 pp.).* Figure 1 shows the unit-cell contents, Figure 2 the atom numbering within the independent half of the molecule.

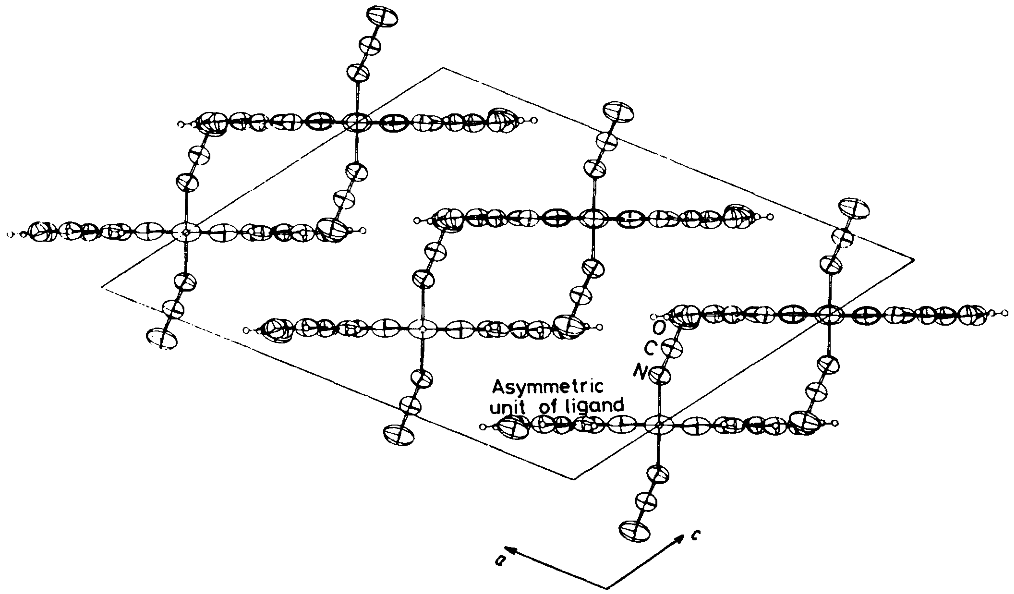

FIGURE 1 Unit-cell contents projected down *b*, showing 20% thermal ellipsoids for the non-hydrogen atoms. Hydrogen atoms are shown with a radius of 0.1 Å

DISCUSSION

The unit-cell contents comprise discrete molecules of the complex $[Co(terpy)(NCO)_2]$, in which the cobalt atom is five-co-ordinated by the three nitrogen atoms of the tridentate terpyridyl ligand and the two nitrogen atoms of the cyanate groups. Each molecule lies astride a crystallographic two-fold axis, so that only one half of it, comprising the asymmetric unit, is crystallographically independent. In Figure 1 this two-fold symmetry of the molecule is clearly seen, as is also the mode of crystal packing which appears to be dominated by tidily interleaving layers of parallel terpyridyl ligand planes. The ligand plane including the cobalt atom lies parallel to *b* and none of the non-hydrogen atoms involved deviates from it by more than 0.02 Å. It is also evident from Figure 1 that the planes of the terpyridyl ligands of successive molecules form successive sheets approximately normal to the *ac* cell diagonal and that the cyanate oxygen atoms of one layer of molecules lie almost exactly in the plane of the next. Figure 3 shows

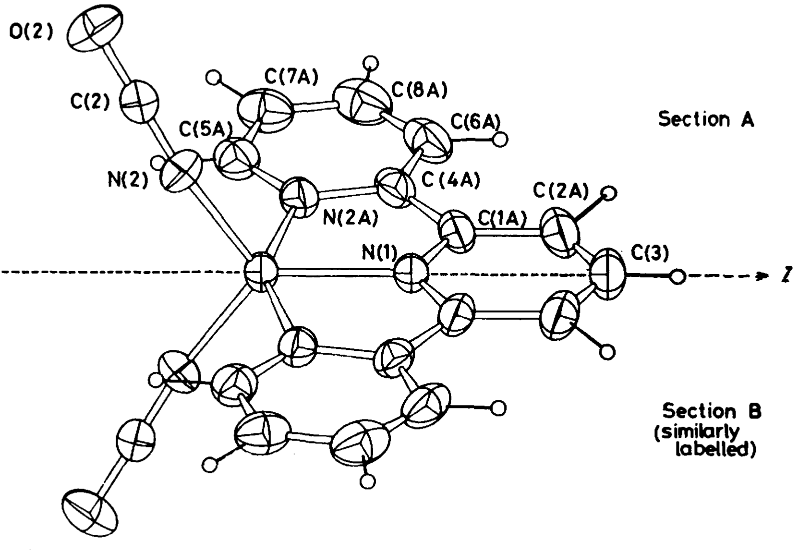

FIGURE 2 Molecular projection (as for Figure 1) showing atom labelling. Hydrogen atoms are numbered according to the carbon atoms to which they are attached

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

a projection of such a sheet of Co(terpy) moieties with the ' coplanar ' cyanate oxygen atoms associated with it tucked into the cavities in the sheet. It will be apparent that the oxygen atom is ' chelated ' by H(2A,6A) of one of the adjacent terpyridyls [H(2A,6A) · · · O(2) $(x, 1-y, z-\frac{1}{2})$ 3.02(9), 2.83(8) Å] on the one side, and H(5A,7A) of another terpyridyl on the other [H(5A,7A) · · · O(2) $(x, \bar{y}, z-\frac{1}{2})$ 2.60(6), 2.64(7) Å] while there is a further contact [H(8A) · · · O(2) $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 2.83(15) Å]. It appears most likely that it is the constraint of these forces that is responsible for the deviation of the Co–N–C angle from 180°; although the disposition of the O(2) atoms in pairs of Figure 3 suggests that O(2) · · · O(2) repulsion may be responsible for the latter distortion and, in fact, the directionality of the distortion is in keeping with this, the relevant O(2) · · · O(2) distance is quite long, being slightly greater than 5 Å.

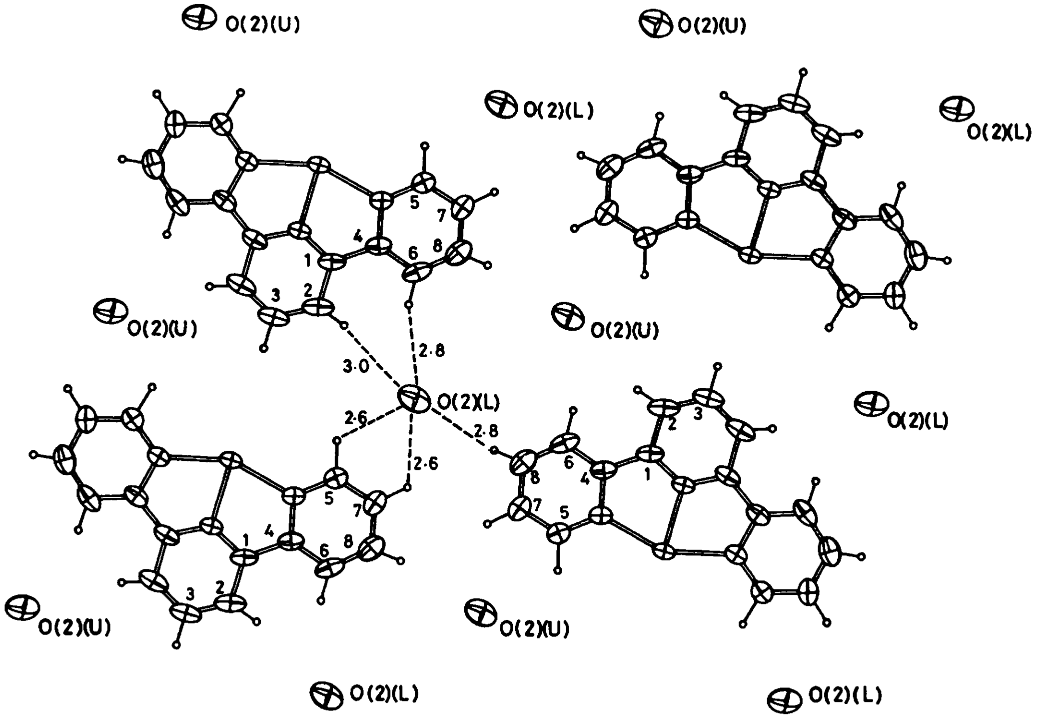


FIGURE 3 Projection of a sheet of successive Co(terpy) fragments showing their packing in the plane, together with the oxygen atoms from molecules in successive upper (U) and lower (L) sheets filling the interstices

TABLE 3

Comparative terpy co-ordination geometries in cobalt(II) complexes (1 B.M. ≈ 9.27×10^{-24} A m^2)

	a	*b*	*c*	*d*	*e*
$\mu_{\text{eff.}}$(300 K)/B.M.	4.8	5.0 [f]	2.9	4.0	0.5
⟨Co–N(1)⟩/Å	2.058	2.09	1.89	1.98, 1.95	1.85
⟨Co–N(2)⟩/Å	2.146	2.15	2.10	2.12, 2.13	1.95
⟨N(2)–Co–N(1)⟩/°	76.2	75	79.2	79.2, 79.8	82.6
⟨N(2)–Co–N(2)⟩/°	152.4	147	158.3	158.3, 159.4	165.1

[a] [Co(terpy)(NCO)$_2$], this work. [b] [Co(terpy)Cl$_2$].[5] [c] [Co(terpy)$_2$]Br$_2$·3H$_2$O; E. N. Maslen, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1974, 1803. [d] [Co(terpy)$_2$][SCN]$_2$, phases 1 and 2; C. L. Raston and A. H. White, *J.C.S. Dalton*, 1976, 7. [e] [Co(terpy)(OH)(CO$_3$)].[8] [f] Ref. 4.

Few examples of cyanate geometries are available in the literature and the present is one of the more precisely determined. It has been suggested previously[13] that there may be a correlation between the magnitude of the X–N–C angle and the N–C distance in cyanate derivatives and complexes. In the present case, the deviation from linearity is large and given the angle of 160° it would be expected that C–N should be *ca.* 1.16 Å; in fact it is much shorter, being 1.126(9) Å. It seems unlikely that the difference can be accounted for on the grounds of lack of correction for libration in the present structure. The Co(terpy) geometry does not differ significantly from that observed in [Co(terpy)Cl$_2$] (Table 3); in the present case, however, the ligand planarity is much more rigorous. {The cobalt atom in [Co(terpy)Cl$_2$] lies 0.42 Å out of the ligand plane.}

An examination of the stereochemistry of compounds of the type [M(tridentate ligand)(unidentate ligand)$_2$] using a repulsion-energy approach has been given,[14] and is extended here. The locations of the symmetrical tridentate ligand ABC, the unidentate ligands D and E, and the axes are defined by specifying that $\phi_{\mathrm{A}} = \phi_{\mathrm{B}} = \phi_{\mathrm{C}}$, $\theta_{\mathrm{B}} = 180.0°$, and $\theta_{\mathrm{C}} = -\theta_{\mathrm{A}}$ (Figure 4). The coordinates of the *i*th atom are ϕ_i, which is defined as the angle between the M–*i* bond and the axis perpendicular to the ABC plane, and θ_i, which is defined as the angle between the plane vertical to ABC incorporating the M–*i* bond and the plane vertical to ABC incorporating M and the midpoint of AC. The geometry of the tridentate ligand is given by two variables, the normalized bite *b* of each chelate ring, and the tridentate angle ABC which is equal to θ_{A}. Two limiting assumptions can be made about the rigidity of the tridentate ligand with respect to the tridentate angle ABC and the interaction between A and C. (*i*) The tridentate ligand is completely flexible. The two arms of the ligand are freely hinged at B, and the repulsion between A and C is included in the total repulsion energy. (*ii*) The tridentate ligand is completely rigid. The tridentate angle ABC is fixed, and hence the repulsion between A and C is constant and may be omitted from the total repulsion energy. In this case ϕ_{A} is also fixed for any given value of *b*, and is given by: $\phi_{\mathrm{A}} = \arcsin[b/2\cos(\theta_{\mathrm{A}}/2)]$.

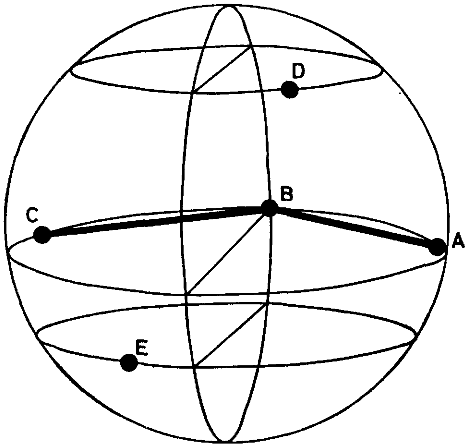


FIGURE 4 General stereochemistry for [M(tridentate ligand)(unidentate ligand)$_2$]

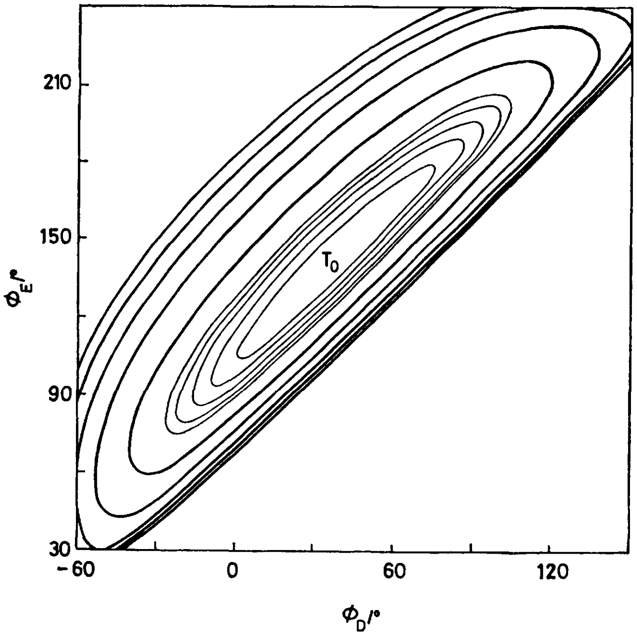


FIGURE 5 Projection of the potential-energy surface for [M(flexible tridentate ligand)(unidentate ligand)$_2$] onto the ϕ_{D}–ϕ_{E} plane. The five faint contour lines are for successive 0.01 increments above the minimum, and the five heavy contour lines are for successive 0.1 increments above the minimum. $b = 0.9$, $n = 6$

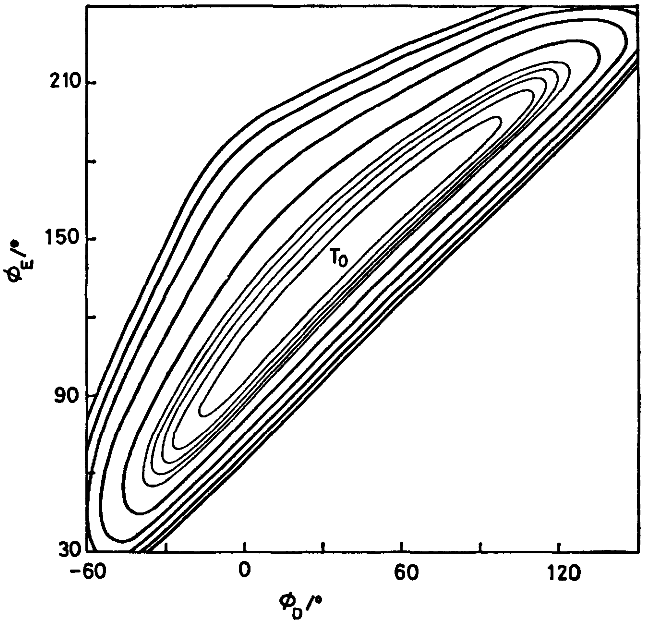


FIGURE 6 Projection as in Figure 1, except that $b = 1.2$

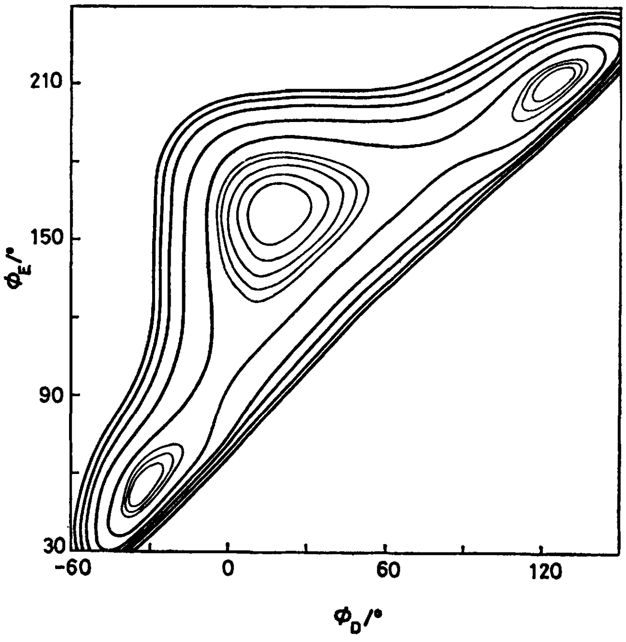


FIGURE 7 Projection as in Figure 1 except that $b = 1.5$

Representative potential-energy surfaces projected onto the ϕ_{D}–ϕ_{E} plane, calculated assuming a flexible tridentate ligand, are shown in Figures 5—7. At low values of the normalized bite the only minimum is at the centre of the potential-energy surface (Figures 5 and 6), but a second minimum develops at high values (Figure 7). The angular co-ordinates corresponding to the first minimum are shown in Figure 8. (The significantly different behaviour reported previously was an artefact due to the lower precision used in those calculations.) This stereochemistry always contains two mirror planes, one through MABC and the other through MBDE, with $\phi_A = 90.0°$ and $\phi_E = 180.0° - \phi_D$. There is a continuous transformation from one co-ordination polyhedron into another as the normalized bite is increased (Figure 9). At $b = 2^{1/2}$, $\phi_D = 30.0°$, $\phi_E = 150.0°$, $\theta_A = 90.0°$, and the stereochemistry is a trigonal bipyramid with the tridentate ligand spanning axial–equatorial–axial sites [Figure 9(*a*)]. At $b = 1.55$, $\phi_D = 11.3°$ $\phi_E = 168.7°$, $\theta_A = 78.7°$, and the stereochemistry is a square pyramid with the tridentate ligand spanning basal-apical-basal sites [Figure 9(*b*)]. At $b = 3^{1/2}$, $\phi_D = 0°$, $\phi_E = 180.0°$, $\theta_A = 60.0°$, and the stereochemistry is a trigonal bipyramid with the tridentate ligand spanning three equatorial sites [Figure 9(*c*)].

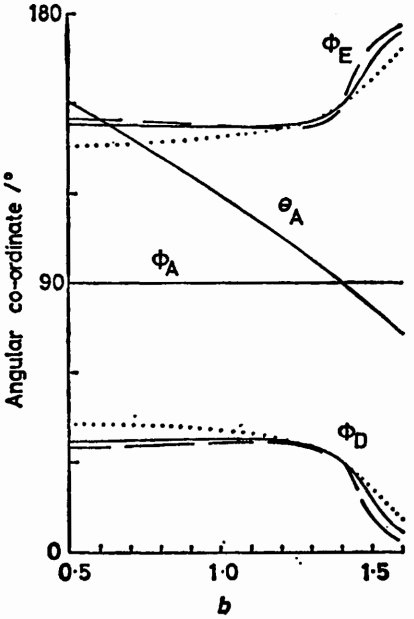


FIGURE 8 Angular co-ordinates for the first stereochemistry of [M(flexible tridentate ligand) (unidentate ligand)$_2$] as a function of normalized bite *b*. *n* = 1 (· · · ·), 6 (——), or 12 (— — —)

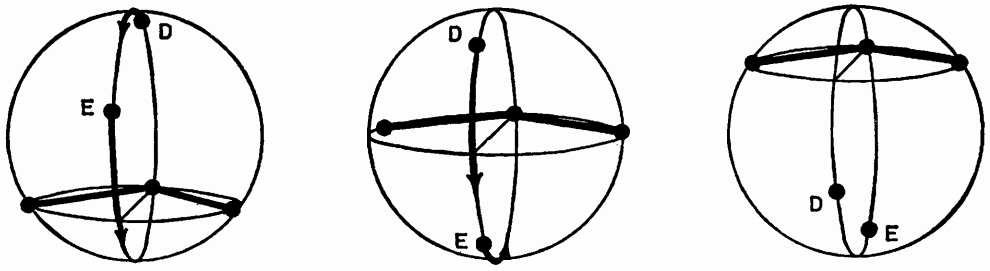
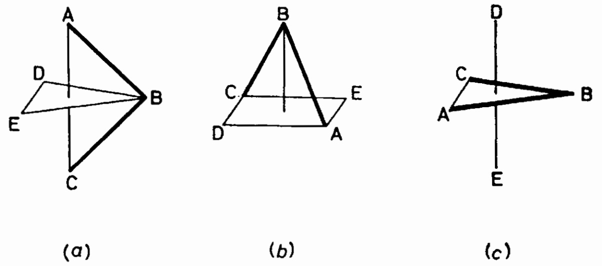


FIGURE 11 Interconversion of stereochemistries of [M(flexible tridentate ligand)(unidentate ligand)$_2$]

The second minimum on the potential-energy surfaces exists as a discrete minimum only above $b = 1.32$. At $b = 2^{1/2}$, $\phi_A = 117°$, $\theta_A = 76°$, $\phi_D = -27°$, $\phi_E = 63°$, and a trigonal bipyramid is formed, in which the tridentate ligand spans equatorial–axial–equatorial sites (Figure 10).



(*a*) (*b*) (*c*)

FIGURE 9 Stereochemistries of [M(tridentate ligand)-(unidentate ligand)$_2$]: $b = 1.414$ (*a*), 1.55 (*b*), and 1.732 (*c*)

An important point to note from the potential-energy surfaces is that the long trough is almost at 45° to the ϕ_D and ϕ_E axes. That is, for $b < \sim 1.4$: $\phi_D - \phi_E =$ DME $\sim$ constant $\sim 100°$. The stereochemical changes which occur on movement along this trough are shown in Figure 11. These changes involve changes in ϕ_A, and hence θ_A, which is equal to the tridentate angle ABC. No tridentate ligand can be completely regarded as being freely hinged at atom B, and according to the design of the particular ligand some preferred value of ABC, and hence θ_A and ϕ_A, will be favoured. This is expected to largely determine the position of the molecule along the

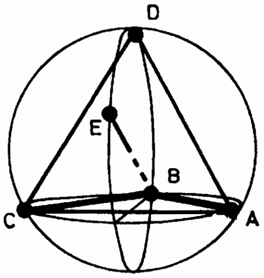


FIGURE 10 Second stereochemistry of [M(tridentate ligand)-(unidentate ligand)$_2$]

trough, the stereochemistry at the centre of the trough having higher values of ABC and θ_A.

Imposing complete rigidity on the tridentate ligand conversely fixes ϕ_A, and allows only a much more restricted variation in ϕ_D and ϕ_E. This is illustrated in Figures 12—14 for three values of ABC, maintaining $b = 1.2$, and should be compared with Figure 6.

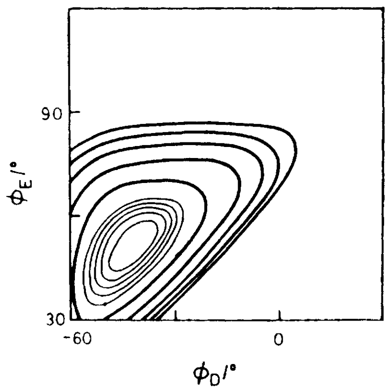


FIGURE 12 Projection of the potential-energy surface for [M(rigid tridentate ligand)(unidentate ligand)$_2$] onto the ϕ_D–ϕ_E plane. The five faint contour lines are for successive 0.01 increments above the minimum, and the five heavy contour lines are for successive 0.1 increments above the minimum. ABC = 60°, $\phi_A = 136.1°$, $b = 1.2$, and $n = 6$

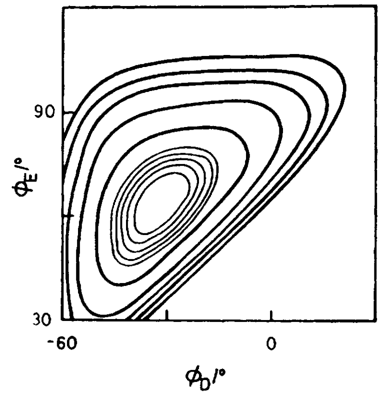


FIGURE 13 Projection as in Figure 12 except that ABC = 80° and $\phi_A = 128.4°$

TABLE 4

Stereochemical parameters for [M(tridentate ligand)(unidentate ligand)$_2$] complexes

Complex	b	θ_A	ϕ_A	ϕ_D	ϕ_E	DME
$[Co\{N(CH_2CH_2NEt_2)_2(CH_2CH_2SMe)\}(NCS)_2]$ [a]	1.22	86	118	−27	72	99
$[Co\{NMe(CH_2CH_2NMe_2)_2\}Cl_2]$ [b]	1.28	93	112	−18	86	104
$[Co\{N(CH_2CH_2NEt_2)_2H\}Cl_2]$ [c]	1.29	84	119	−36	67	102
$[Ni\{N(CH_2CH_2AsPh_2)(CH_2CH_2NEt_2)_2\}(NCS)_2]$ [d]	1.32	96	99	−1	100	100
$[Cd\{NMe(CH_2CH_2NMe_2)_2\}(NCS)_2]$ [e]	1.25	97	110	−7	97	104
$[Ge\{S(CH_2CH_2S)_2\}Cl_2]$ [f]	1.29	85	119	−38	60	98
$[Ge\{O(CH_2CH_2S)_2\}Cl_2]$ [g]	1.30	88	115	−29	74	102
$[Sn\{S(CH_2CH_2S)_2\}Cl_2]$ [h]	1.33	84	116	−31	65	96
$[Sn\{O(CH_2CH_2S)_2\}Cl_2]$ [i]	1.29	93	111	−22	78	100
$[Cd(terpy)\{Mn(CO)_5\}_2]$ [j]	1.10	114	90	22	155	132
$[Zn(terpy)Cl_2]$ [k]	1.20	106	98	7	119	112
$[Co(terpy)Cl_2]$ [l]	1.22	104	99	0	111	111
$[Co(terpy)(NCO)_2]$ [m]	1.23	104	90	35	145	111
$[Ni\{N(CH_2C_5H_3MeN)_2H\}Br_2]$ [n]	1.31	98	93	6	155	149
$[Cd\{NC_5H_3(CMe{=}NC_6H_4SMe)_2\}I_2]$ [o]	1.11	112	90	23	143	119
$Cs[V\{NC_5H_3(CO_2)_2\}O_2]\cdot H_2O$ [p]	1.22	104	95	27	136	110

Units of θ, ϕ, and DME are degrees.

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Those molecules of the type [M(tridentate ligand)(unidentate ligand)$_2$] whose structures are known are listed in Table 4. The list has been restricted to tridentate ligands which are symmetrical, and to complexes containing two equivalent unidentate ligands. The variation of ϕ_D and ϕ_E (Table 4) is displayed in Figure 15, and should be compared with the calculated potential-energy surfaces. The complexes are divided into two groups. In the first group, denoted by open circles in Figure 15, the angle between the two metal–unidentate ligand bonds, DME = $\phi_E - \phi_D$, is *ca.* 100° as predicted. In these cases the tridentate ligands are based on flexible aliphatic chains with ABC = θ_A = 84—97°, and are of the type $RA(CH_2CH_2AR_2)_2$ (where A is N or P) or $X(CH_2CH_2X^-)_2$ (where X is O or S). The second group of complexes, denoted as filled circles in Figure 15, contain much more rigid tridentate ligands, in which the ligand design enforces a larger tridentate angle ABC, and hence stereochemistries closer to the centre of the potential-energy surface. These complexes have significantly greater angles between the two metal–unidentate ligand bonds, $\phi_D - \phi_E$ = DME, which can be attributed to two effects. First, bulky unidentate ligands will increase this angle, the most extreme example being $[Cd(terpy)\{Mn(CO)_5\}_2]$. Secondly, the presence of bulky substituents in the metal–tridentate ligand plane forces the unidentate ligands apart, as in [Ni{N(CH$_2$C$_5$H$_3$Me-

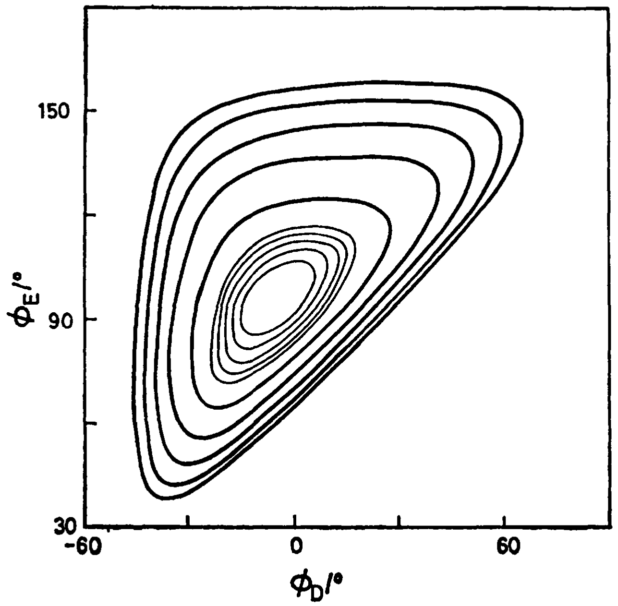

FIGURE 14 Projection as in Figure 12 except that ABC = 100° and $\phi_A = 111.0°$

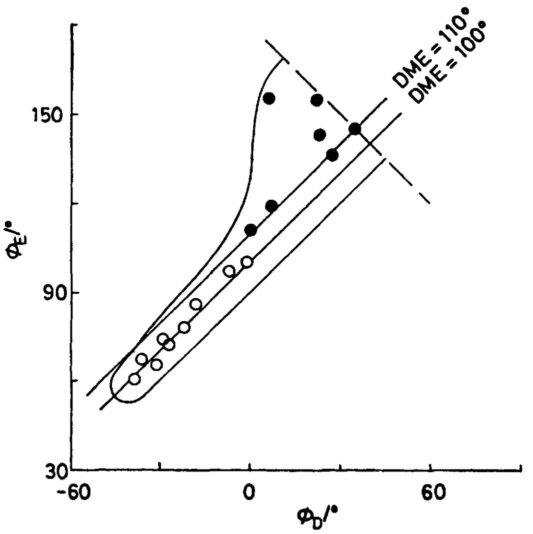

FIGURE 15 Angular co-ordinates for molecules of the type [M(tridentate ligand)(unidentate ligand)$_2$]

N)$_2$H}Br$_2$] and [Cd{NC$_5$H$_3$(CMe=NC$_6$H$_4$SMe)$_2$}I$_2$]. A similar but smaller effect attributable to the hydrogen atoms is present in the terpyridyl complexes, $\phi_D - \phi_E =$ DME $\sim$ 110°. In contrast the tridentate ligands in the first group of compounds have tetrahedrally co-ordinated terminal donor atoms, and there are no in-plane interactions of this type.

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