Stereochemistry of [M(bidentate ligand)$_2$(unidentate ligand)]. Crystal Structure of Iodobis(pyrrolidinyldithiocarbamato)iron(III)–Iodine (2/1)

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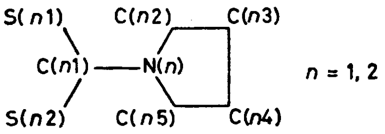
The crystal structure of a complex analysing as FeL_2I_2, L = pyrrolidinyldithiocarbamate, has been determined at 295(1) K by *X*-ray diffraction and refined to a residual of 0.046 for 1 422 ' observed ' reflections. Crystals are monoclinic, $P2_1/c$, a = 6.735(4), b = 18.28(2), c = 15.11(1) Å, β = 96.71(5)°, and Z = 4. The substance has been shown to be a molecular complex, $[FeI\{S_2CN(CH_2)_4\}_2]\cdot 0.5\,I_2$, the iodine molecule being located on a crystallographic centre of symmetry. The bond lengths are as expected [Fe–I 2.652(3), Fe–S 2.271(4)—2.305(5) Å]; for the iodine molecule, I–I is 2.779(3) Å. The latter has a contact at 3.516(3) Å to the complexed iodine atom. The stereochemistry of the five-co-ordinate complex is a square pyramid with the iodine atom in the apical site, distorted towards a square pyramid with the iodine atom in a basal site. This distortion is discussed in terms of repulsion theory.

REACTION of complexes of the type $[FeI(S_2CNR_2)]$ with iodine has been reported to yield products of the type $[FeI_2(S_2CNR_2)_2]$;[1] the nature of these compounds remains somewhat uncertain although it has been suggested that they may be adducts of the type $[FeI(S_2CNR_2)_2]\cdot 0.5I_2$. If so, it is interesting that this formulation persists through complexes with a wide range of ligand substituents. In order to determine unambiguously the nature of these complexes, we have determined the crystal structure of one of them containing the pyrrolidinyldithiocarbamate ligand; the preparation followed that reported previously.[1]

EXPERIMENTAL

Crystal Data.—$C_{10}H_{16}FeI_2N_2S_4$, M = 602.2, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 6.735(4), b = 18.28(2), c = 15.11(1) Å, β = 96.71(5)°, U = 1 847(2) Å^3, D_m = 2.14(1), Z = 4, D_c = 2.16$_5$ g cm^{-3}, $F(000)$ = 1 144, specimen size 0.10 × 0.06 × 0.22 mm, monochromatic Mo-K_α radiation (λ = 0.710 6$_9$ Å), μ = 43.4 cm^{-1}, T = 295(1) K.

Structure Determination.—A unique data set to $2\theta_{max.}$ = 50° (terminated during h = 5 due to machine failure) was measured on a Syntex $P\bar{1}$ four-circle diffractometer, in the conventional θ—2θ scan mode, yielding 2 661 independent reflections, 1 422 of which with $I > 3\sigma(I)$ being considered ' observed ' and used in the least-squares refinement after absorption correction and solution of the structure by direct methods. The parameters of FeI_2S_4 were refined jointly in a single block; other non-hydrogen atoms were refined as 9 × 9 blocks with anisotropic thermal motion.



Hydrogen-atom parameters were constrained estimates, U_H (isotropic) being set at ⟨1.25 U_{ii} (parent C)⟩. The values of the residuals(R and R') were 0.046 and 0.047 respectively with reflection weights $[\sigma^2(F_o) + 0.000\,3(F_o)^2]^{-1}$. Scattering factors for the neutral atoms were employed, those of the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[2-4] Computations were carried out using the ' *X*-RAY '76 ' program system [5] on a CYBER 76 computer. Structure factor amplitudes, thermal parameters, and hydrogen-atom parameters are deposited as Supplementary Publication No. SUP 22795 (13 pp.).† Non-hydrogen-atom fractional cell co-ordinates are given in Table 1. Non-hydrogen-atom numbering with ligands n = 1 and 2 is as shown; hydrogen atoms are designated A,B for distinguishing purposes.

TABLE 1

Non-hydrogen-atom fractional cell co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
I(1)	0.169 0(2)	0.222 8(1)	0.173 4(1)
I(2)	0.042 5(2)	0.062 5(1)	0.050 9(1)
Fe(1)	−0.015 2(3)	0.320 0(1)	0.062 3(1)
S(11)	−0.331 1(6)	0.271 5(2)	0.046 2(3)
S(12)	−0.032 0(6)	0.262 4(2)	−0.071 5(2)
S(21)	−0.077 7(6)	0.420 9(2)	0.146 4(2)
S(22)	0.225 4(6)	0.401 1(2)	0.031 8(2)
C(11)	−0.258 1(19)	0.231 1(7)	−0.049 4(9)
N(11)	−0.367 5(16)	0.182 9(6)	−0.096 5(7)
C(12)	−0.556 6(24)	0.153 1(10)	−0.075 4(11)
C(13)	−0.611 9(29)	0.098 0(13)	−0.140 3(14)
C(14)	−0.475 4(26)	0.098 8(11)	−0.207 1(13)
C(15)	−0.303 9(24)	0.150 7(9)	−0.178 4(9)
C(21)	0.137 1(19)	0.457 6(6)	0.110 5(8)
N(21)	0.221 3(16)	0.516 8(5)	0.139 7(7)
C(22)	0.151 6(24)	0.562 9(8)	0.209 5(9)
C(23)	0.341 5(23)	0.605 0(8)	0.244 9(9)
C(24)	0.475 0(26)	0.605 7(10)	0.174 0(11)
C(25)	0.404 0(21)	0.546 1(7)	0.108 6(9)

RESULTS AND DISCUSSION

The crystal-structure determination effectively confirms the stoicheiometry of the complex as being $[FeI\{S_2CN(CH_2)_4\}_2]\cdot 0.5I_2$. The unit-cell contents, shown in projection down a in Figure 1, contain $[FeI\{S_2CN(CH_2)_4\}_2]$ and I_2 molecules; the latter is located about an inversion centre so that only one of the iodine atoms is independent. The two molecular species are not strictly ' discrete ' as there appears to be an interaction between the iodine molecule and the iodine atom of the complex, presumably of a charge-transfer nature, the I ··· I distance being 3.516(3) Å. The I–I distance within the

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

molecular iodine is considerably longer [2.779(3) Å] than in free iodine (2.66$_7$ Å).[6] The I–I ··· I angle is 177.16(6)°, while the I ··· I–Fe angle is 99.12(8)°. The bond Fe–I [2.652(3) Å] may be somewhat longer than the less precisely determined value observed in [FeI(S$_2$CNEt$_2$)$_2$] [2.59(1) Å].[7] The overall result is a loose 'dimeric' association of the type (R$_2$NCS$_2$)$_2$FeI ··· I–I ··· IFe(S$_2$CNR$_2$)$_2$.

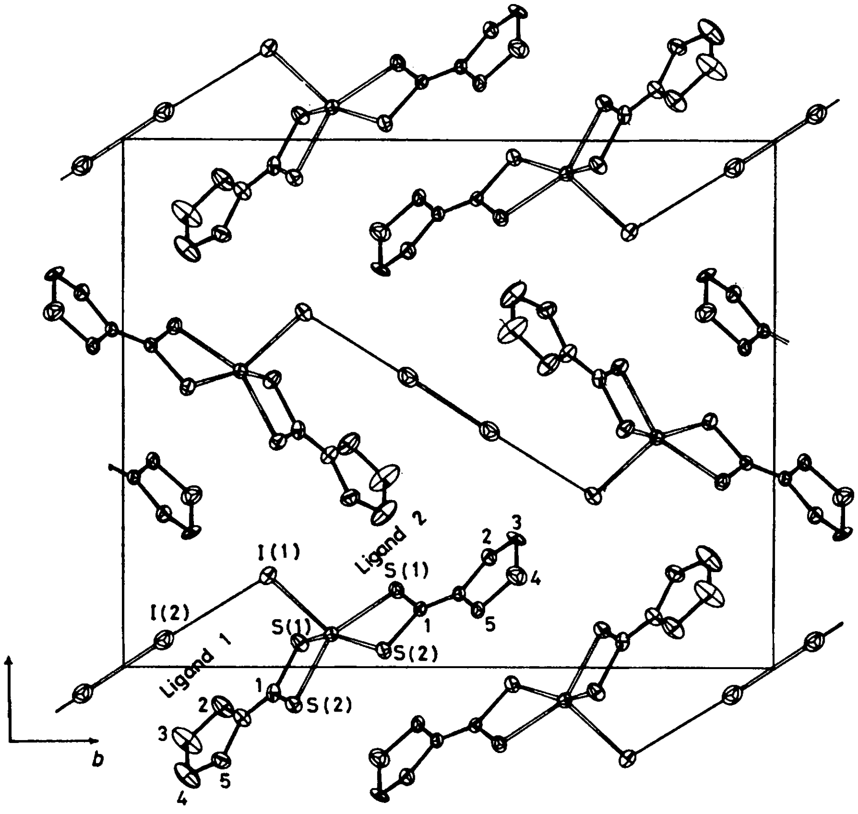
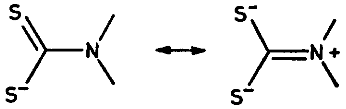


FIGURE 1 Unit-cell contents projected down *a* showing 20% thermal ellipsoids for the non-hydrogen atoms, together with atom labelling

Within the [FeI{S$_2$CN(CH$_2$)$_4$}$_2$] species the molecular geometry (Table 2) is as expected. The bond lengths of Fe–S show a rather wide scatter [2.271(4)—2.305(5) Å] as is often the case in FeX(S$_2$CNR$_2$)$_2$ complexes, as is the variation in I–Fe–S angles [99.6(1)—106.8(1) Å]. In the present case, however, the scatter appears to originate in distortions of a less random nature than those previously observed and ascribed to 'packing forces'. The interaction between the molecular I$_2$ and the complexed iodine atom lies almost normal to the Fe–I bond and is directed outwards near the 'axis' of ligand 1. The I–Fe–S(1, 2) angles of ligand 1 [99.6(1), 102.9(1)°] are less than those of ligand 2 [106.8(1), 105.8(1)°], indicative of a possible attractive interaction between the two independent iodine species against crystal packing forces and this is reflected in the associated I ··· S distances of 3.784(5), 3.857(5) Å (ligand 1), 3.986(5), 3.941(5) Å (ligand 2). The molecular iodine atom, moreover, is in reasonably close proximity to the conjugated section of ligand 1, and its neighbouring protons, a result which is not surprising in view of the tendency of the dithiocarbamate ligand to delocalize positive charge from the metal to the nitrogen. The lengths of I(2) ··· S(1, 2), C(1), N(1), and H(5A) are 4.569(5), 4.099(5), 3.89(1), 4.00(1), and 3.6$_5$ Å respectively, while the inversion related I(2) has distances of 3.8$_4$ and 3.9$_4$ Å to H(4A, 5A) respectively. The vibrational amplitudes of the carbon atoms of the pyrrolidine ring of ligand 1 are much larger than those of ligand 2 (Figure 1) and the ring more nearly planar (Table 3), suggesting that in reality the ring atoms of ligand 1 are disordered and that this disorder may be induced by the proximity of the iodine molecule, either as a consequence of I ··· H interactions and/or the inability of the ring to adopt its usual conformation because of obstruction by the iodine position. Ligand 2 is more normal in respect of conformation (Table 3).



As usual, the iron lies well out (0.55 Å) of the plane defined by the four sulphur atoms [deviations: S(11, 12, 21, 22), −0.04, 0.04, 0.04, −0.04 Å]; the inclinations of the ligand planes to this plane, however, are unusually shallow (8.4, 8.0° respectively for 1,2) and the iron atom lies 0.31 Å out of the planes of both ligands. (The dihedral angle between the two ligand planes is 16.3°.) While the unusual disposition (in this respect) of ligand 1 might be ascribed to interaction with the iodine molecule (see above), the reason for the disposition of ligand 2 is not so apparent. In fact (Table 4) although the diversity of the $FeXS_4$ core parameters is large, it would seem that at least among the halogen substituents, the number of structures determined is now sufficient to discern a possible trend in deviations of the iron atom from the S_4 plane [greatest for Cl (*ca.* 0.65 Å), least for I (*ca.* 0.55 Å)], accompanied by a parallel diminution in the dihedral angle between the two ligand planes.

TABLE 2

Molecular non-hydrogen geometry [*]

(*a*) Distances (Å)

Fe–I(1)	2.652(3)	C(1)–N(1)	1.30(2), 1.28(2)
Fe–S(1)	2.292(5), 2.305(5)	N(1)–C(2)	1.45(2), 1.47(2)
Fe–S(2)	2.271(4), 2.282(5)	N(1)–C(5)	1.48(2), 1.47(2)
S(1) · · · S(2)	2.843(6), 2.849(6)	C(2)–C(3)	1.42(3), 1.53(2)
S(1)–C(1)	1.74(1), 1.74(1)	C(3)–C(4)	1.44(3), 1.48(2)
S(2)–C(1)	1.70(1), 1.73(1)	C(4)–C(5)	1.52(2), 1.51(2)

(*b*) Angles (°)

I(1)–Fe–S(1)	99.6(1), 106.8(1)
I(1)–Fe–S(2)	102.9(1), 105.8(1)
S(1)–Fe–S(2)	77.1(2), 76.8(2)
S(1)–Fe–S(1)	98.1(2)
S(2)–Fe–S(2′)	94.8(2)
S(1)–Fe–S(2′)	154.5(2), 150.3(2)
Fe–S(1)–C(1)	84.5(5), 85.7(4)
Fe–S(2)–C(1)	86.2(5), 86.6(4)
S(1)–C(1)–S(2)	111.5(7), 110.4(7)
S(1)–C(1)–N(1)	122(1), 125(1)
S(2)–C(1)–N(1)	126(1), 125(1)
C(1)–N(1)–C(2)	126(1), 125(1)
C(1)–N(1)–C(5)	122(1), 124(1)
C(2)–N(1)–C(5)	112(1), 112(1)
N(1)–C(2)–C(3)	106(1), 102(1)
C(2)–C(3)–C(4)	110(2), 108(1)
C(3)–C(4)–C(5)	109(2), 107(1)
C(4)–C(5)–N(1)	102(1), 106(1)

[*] Where two entries are given these are for ligands 1 and 2 respectively.

TABLE 3

Least-squares planes, defined by the S_2CNC_2 fragments of the two dithiocarbamate ligands, in the form $pX + qY + rZ = s$, relative to the orthogonal right-hand angström frame (X, Y, Z) defined with X parallel to a and Z in the ac plane. Atom deviations, δ, and σ(defining atoms) are given in Å

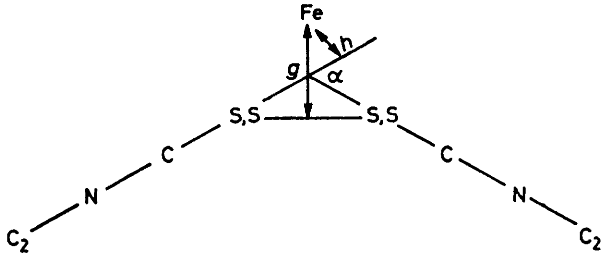
	Ligand 1	Ligand 2
10^4p	−4 034	4 761
10^4q	7 317	−5 126
10^4r	−5 495	7 146
s	4.161	−2.741
σ	0.02	0.02
δS(1)	0.02	−0.01
δS(2)	−0.03	0.02
δC(1)	0.00	−0.02
δN(1)	0.01	−0.01
δC(2)	−0.03	0.02
δC(3)	−0.13	0.59
δC(4)	0.01	0.31
δC(5)	0.02	−0.01
δFe	−0.31	0.31

Calculations based on the minimisation of the total repulsion energy have previously been reported[8] for complexes of the type [M(bidentate)$_2$(unidentate)]. These calculations showed that for small values of the normalized bite ($b < 1.2$) a single minimum on the potential-energy surface corresponds to the square pyramid (or more correctly, the rectangular pyramid). As the normalized bite is progressively increased, the minimum becomes shallower and then symmetrically splits into two minima corresponding to the two equivalent irregular trigonal bipyramids. These two minima progressively deepen and move further apart as the normalized bite is further increased.

A number of effects can be predicted as the value of the effective bond-length ratio R(unidentate/bidentate) is varied, which is defined as the distance between the central atom and the effective centre of repulsion of the metal–unidentate ligand bond, divided by the distance between the central atom and the effective centre of repulsion of the metal–bidentate ligand bond. The break from the rectangular pyramid to the trigonal bipyramid occurs at higher values of b as R(unidentate/bidentate) is decreased from 1.0 to 0.6, but this behaviour is reversed at still lower values of R(unidentate/bidentate). The variation of the unidentate–M–bidentate bond angles with b and R(unidentate/bidentate) is shown in Figure 2. The stabilisation of the square pyramid relative to the trigonal bipyramid for R(unidentate/bidentate) <1.0 is similar to the behaviour observed for [M(unidentate A)$_4$(unidentate B)].[9]

TABLE 4

Interplanar angles (°) and atom deviations (Å) observed in a variety of $FeX(S_2CNR_2)_2$ structure determinations



Compound	g	h	α
[FeCl(S$_2$CNEt$_2$)$_2$] [a]	0.64	0.30, 0.08	51.7
[FeCl(S$_2$CNPr$^i_2$)$_2$]·CHCl$_3$ [b]	0.65	0.01, 0.06	45.2
[FeBr(S$_2$CNEt$_2$)$_2$] [c]	0.63	0.14, 0.05	45.2
[FeI(S$_2$CNEt$_2$)$_2$] [d]	0.59	0.23, 0.00	32.1
[FeI{S$_2$CN(CH$_2$)$_4$}$_2$]·0.5I$_2$ [e]	0.55	0.31, 0.31	16.3
[Fe(NCS)(S$_2$CNEt$_2$)$_2$] [f]	0.57	0.02, 0.15	30.8
[Fe(NO)(S$_2$CNMe$_2$)$_2$] [g]	0.63	0.09, 0.20	30.9

[a] The data given for [FeCl(S$_2$CNEt$_2$)$_2$] are based on a recent diffractometer data redetermination of that structure, confirming the essential details of the original determination [B. F. Hoskins and A. H. White, *J. Chem. Soc.* (*A*), 1970, 1668]. [b] S. Mitra, B. N. Figgis, C. L. Raston, B. W. Skelton, and A. H. White, *J.C.S. Dalton*, 1979, 753. [c] G. E. Chapps, S. W. McCann, H. H. Wickman, and R. C. Sherwood, *J. Chem. Phys.*, 1974, **60**, 990. [d] Ref. 7. [e] This work. [f] C. L. Raston, W. E. Sly, and A. H. White, *Austral. J. Chem.*, 1980, **33**, 221. [g] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Ouston, *J. Chem. Soc.* (*A*), 1970, 1275.

The general stereochemistry for [M(bidentate)$_2$(unidentate)], with no assumed symmetry, is shown in Figure 3. The axes are chosen so that $\phi_A = \phi_B = \phi_C$ and $\theta_B = 180°$, and the structure is completely defined by ϕ_A, θ_A, θ_C, ϕ_D, and ϕ_E, the remaining variables θ_D and θ_E being calculated from the normalized bite.

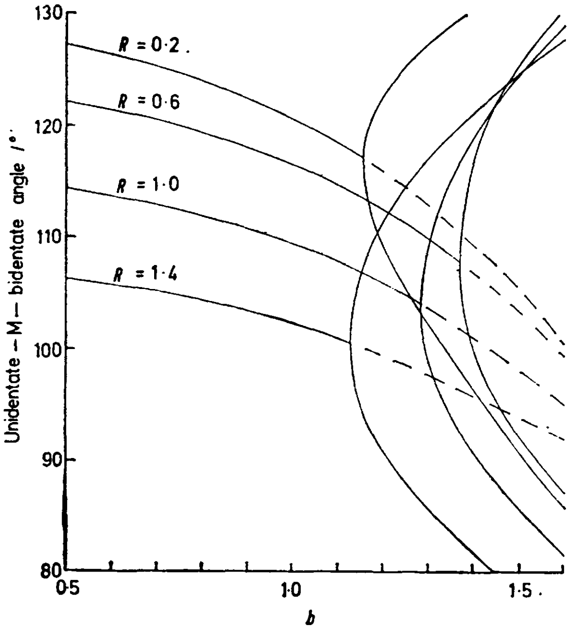


FIGURE 2 Unidentate–M–bidentate bond angles, in degrees, for [M(bidentate)$_2$(unidentate)] as a function of normalized bite b and effective bond-length ratio R(unidentate/bidentate), $n = 6$ (ref. 8).

A typical potential-energy surface, projected onto the ϕ_D—ϕ_E plane, is shown in Figure 4. The potential-energy surface is symmetrical across the lines $\phi_D = \phi_E$, and $\phi_E = 180°$. The blank area centred on $\phi_D = 0$, $\phi_E = 180°$, is because the bidentate ligands cannot span from E to A and from D to C while maintaining $\phi_A = \phi_C$.

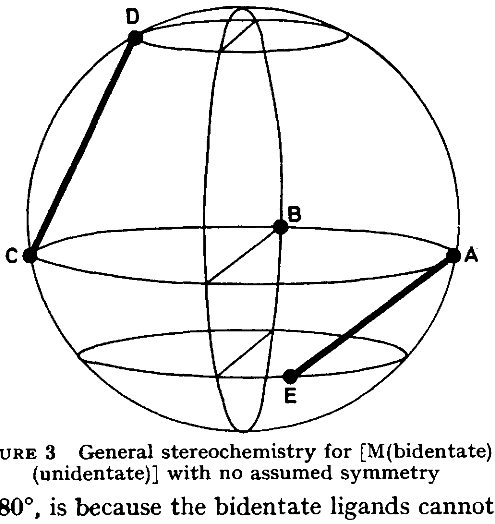


FIGURE 3 General stereochemistry for [M(bidentate)$_2$(unidentate)] with no assumed symmetry

The stereochemistries corresponding to the points marked I, II, and III on Figure 4 are shown in Figure 5. The minimum at I at $\phi_D = 180° — \phi_E = 20.3°$ and $\phi_A = 90°$ is the same as that found previously.[8] Movement along the line $\phi_D = 180° — \phi_E$ in Figure 4 maintains $\phi_A = 90°$ and the two-fold axis through B, and corresponds to movement along the trough in the potential-energy surface reported previously.[8] However the potential-energy surface in Figure 4 also shows that distortions with loss of the two-fold axis are possible, in the direction towards the distorted square pyramid at II. This distorted square pyramid at II can form the symmetrical square pyramid either at I or at III by interchanging the A and E labels on the bidentate AE.

This change from the symmetrical square pyramid at I to the unsymmetrical square pyramid at II can alternatively be conveniently pictured as rotation of one of the bidentate ligands above the triangular plane formed by the unidentate ligand and the other bidentate ligand (Figure 6).

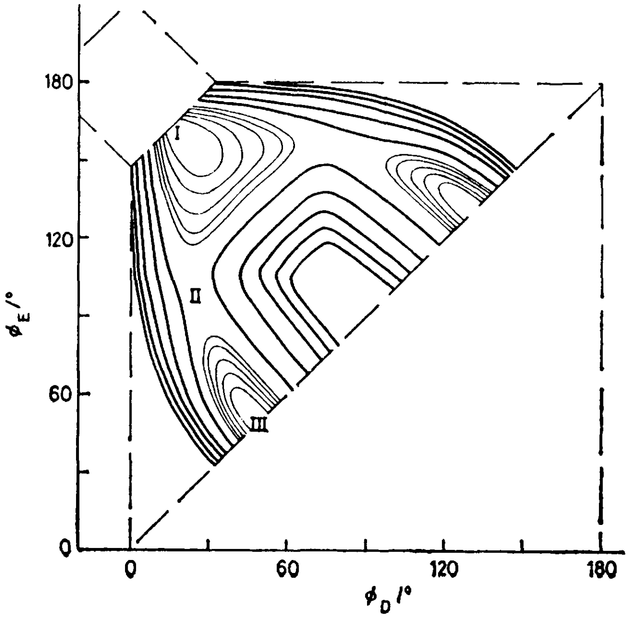


FIGURE 4 Projection of the potential-energy surface for [M(bidentate)$_2$(unidentate)] onto the ϕ_D—ϕ_E plane (in degrees). The five faint contour lines are for successive 0.01 increments above the minima, and the five heavy contour lines are for successive 0.1 increments above the minima, $b = 1.2$, $n = 6$

The unsymmetrical square pyramid at II with the unidentate ligand in a basal site becomes increasingly possible as the metal–unidentate ligand effective bond length is increased relative to the metal–bidentate ligand effective bond length. Potential-energy surfaces for R(unidentate/bidentate) = 1.2 and 1.4 are shown in Figures 7 and 8 respectively. That is, under conditions of one extended bond and four contracted bonds, this unsymmetrical square pyramid, or some intermediate structure, may be expected.

Compounds of the type [M(bidentate)$_2$(unidentate)] containing symmetrical bidentate ligands are listed in Table 5. The four unidentate–metal–bidentate bond angles are listed, the lowest value being defined as BMA.

The first group of compounds are those of phosphorus(v) and arsenic(v). All have a reasonable two-fold axis, that is BMA ~ BMC and BME ~ BMD, and the stereochemistries range from near square pyramidal (BMA = BMC = BME = BMD) to near trigonal bipyramidal (BMA = BMC = 90°, BME = BMD = 120°).

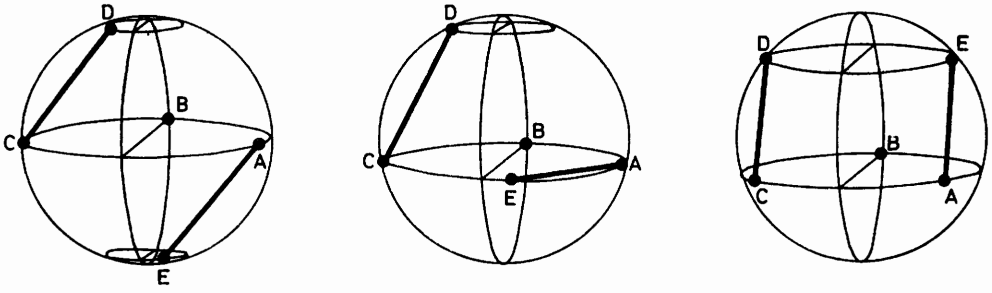


FIGURE 5 Stereochemistries corresponding to points marked on Figure 4

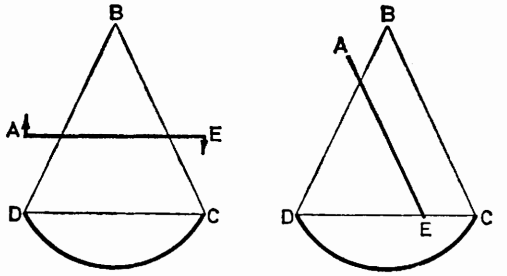


FIGURE 6 Alternative view of stereochemistries corresponding to points marked on Figure 4

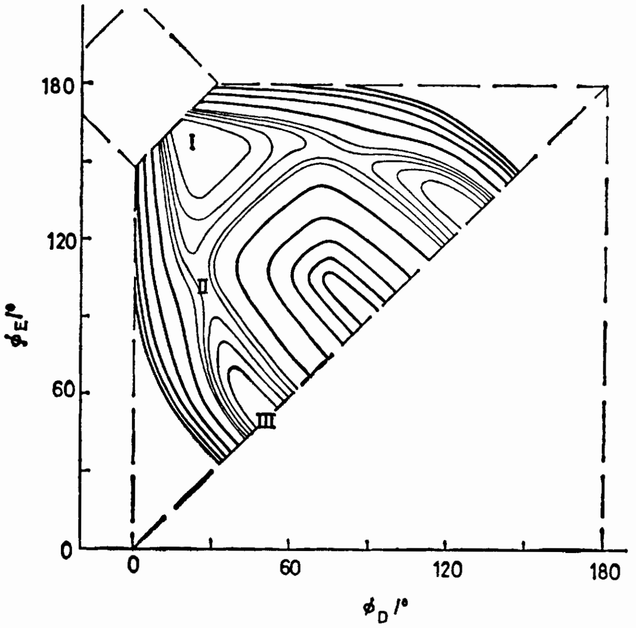


FIGURE 7 Projection of the potential-energy surface for [M(bidentate)$_2$(unidentate)] onto the ϕ_D—ϕ_E plane (in degrees). The five faint contour lines are for successive 0.01 increments above the minima, and the five heavy contour lines are for successive 0.1 increments above the minima, R = 1.2, b = 1.2, n = 6

The experimental bond angles can be fitted against bond angles calculated as a function of the effective bond length of the unidentate ligands relative to the bidentate ligands, Figure 2, to yield R(unidentate/bidentate) = 1.0 for $P(O_2C_6H_4)_2F$, and R(unidentate/bidentate) ~ 0.8 for all other complexes. This difference between fluoro and alkyl derivatives is typical for non-metals bonded to these ligands.[10]

The next five compounds in Table 5 are transition-metal complexes containing oxide or nitride as the unidentate ligand. All are close to square-pyramidal stereochemistry as expected for O^{2-} and N^{3-} with small metal–ligand effective bond-length ratios, and the experimental bond angles can be fitted to calculations based on R(unidentate/bidentate) = 0.8 (Figure 2).

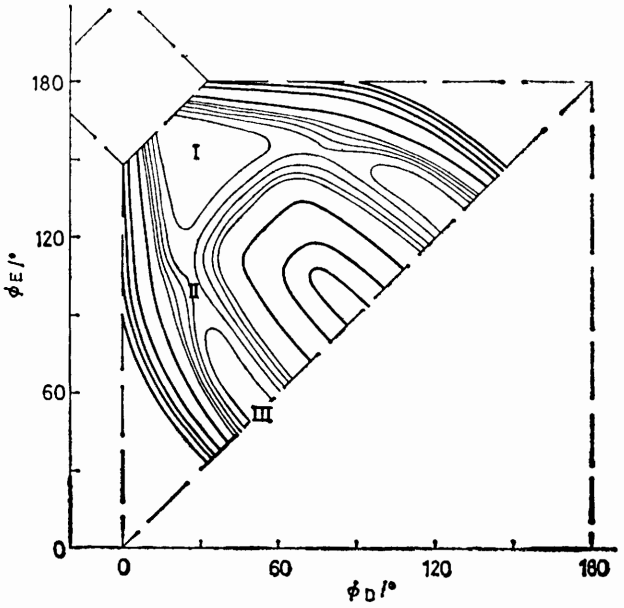


FIGURE 8 Projection of the potential-energy surface for [M(bidentate)$_2$(unidentate)] onto the ϕ_D—ϕ_E plane (in degrees). The five faint contour lines are for successive 0.01 increments above the minima, and the five heavy contour lines are for successive 0.1 increments above the minima, R = 1.4, b = 1.2, n = 6

TABLE 5

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

Complex	*b*	BMA/°	BME/°	BMC/°	BMD/°
$P(O_2C_6H_4)_2F$ [a]	1.43	95.8	106.6	96.0	107.3
$P(O_2C_6H_4)_2Cl$ [b]	1.42	98.8	105.3	98.3	105.0
$P(O_2C_6H_4)_2Ph$ [c]	1.42	99.9	106.1	100.0	108.7
$P(O_2C_6H_4)_2Me$ [d]	1.42	101.0	106.2	102.1	105.6
	1.41	101.4	105.9	102.3	106.4
$P(O_2C_6H_4)_2(CMe_3)$ [e]	1.40	102.5	106.4	102.7	106.6
$As(O_2C_6H_4)_2Me$ [f]	1.40	100.2	108.6	101.1	108.3
$As(OCMe_2CMe_2O)_2Ph$ [g]	1.39	94.5	117.4	95.7	118.0
$As(OCH_2CH_2O)_2(OH)$ [g]	1.40	96.3	109.1	99.4	110.5
$P(S_2C_6H_4)_2Me$ [h]		101.0	108.3		
$[V(MeCOCHCOMe)_2O]$ [i]	1.38	104.8	106.2	105.6	108.4
$[Os(OCH_2CH_2O)_2O]$ [j]	1.33	107.3	112.8	107.3	112.8
$[V(S_2CNEt_2)_2O]$ [k]	1.21	107.4	108.3	107.4	110.2
$[Mo(S_2CNPr_2)_2O]$ [l]	1.18	108.3	109.6	111.7	110.3
$[Re(S_2CNEt_2)_2N]$ [m]	1.19	106.8	107.1	107.9	109.1
$[Fe\{S_2C_2(CF_3)_2\}_2(AsPh_3)]$ [n]	1.41	92.3	101.0	98.2	93.5
$[Fe(S_2C_2Ph_2)_2\{P(OMe)_3\}]$ [o]	1.40	90.3	103.7	106.9	95.2
$[Fe(MeCOCHCOMe)_2Cl]$ [p]		*ca.* 105	*ca.* 105	*ca.* 105	*ca.* 105
$[Fe\{C_6H_4(AsMe_2)_2\}_2(NO)][ClO_4]_2$ [q]	1.34	95.9	98.8	99.1	97.1
$[Fe(S_2CNEt_2)_2Cl]$ [r]	1.24	105.1	105.5	106.7	105.4
$[Fe(S_2CNEt_2)_2Br]$ [s]	1.23	104.7	105.5	105.7	106.0
$[Fe(S_2CNEt_2)_2I]$ [t]	1.23	99.4	107.8	103.1	109.9
$[Fe\{S_2CN(CH_2)_4\}_2I]\cdot 0.5I_2$ [u]	1.24	99.6	102.9	105.8	106.8
$[Fe(S_2CNPr_2)_2Cl]\cdot CHCl_3$ [v]	1.23	104.2	104.6	109.5	107.7
$[Fe(S_2CNEt_2)_2(NCS)]$ [w]	1.24	102.7	103.1	105.5	107.0
$[Fe(S_2CNMe_2)_2(NO)]$ [x]	1.23	103.1	104.3	108.3	107.5
$[Fe(S_2CNEt_2)_2(NO)]$ [y]	1.23	*ca.* 106	*ca.* 106	*ca.* 106	*ca.* 106
$[Co\{C_6H_4(AsMe_2)_2\}_2(NO)][ClO_4]_2$ [z]	1.36	90.3	135.5	92.1	125.2
$[Co(Ph_2PCH_2CH_2PPh_2)_2Cl][SnCl_3]$ [aa]	1.32	90.0	95.8	94.5	94.0
$[Co(Ph_2PCH_2CH_2PPh_2)_2Cl][SnCl_3]\cdot PhCl$ [aa]	1.30	91.7	128.1	92.1	126.1
$[Co\{NH(CH_2CH_2CH_2)_2NH\}_2Cl]Cl\cdot EtOH$ [bb]					
$[Co(S_2CNMe_2)_2(NO)]$ [cc]	1.24	102.2	103.6	103.5	103.5
$[Ni(S_2PEt_2)_2(NC_9H_7)]$ [dd]	1.32	99.7	100.7	98.9	110.3
$[Cu(NH_2CH_2CH_2CH_2NH_2)_2(NCS)][ClO_4]$ [ee]	1.42	89.5	116.8	90.2	109.0
$[Cu(bipy)_2(NO_3)][NO_3]\cdot H_2O$ [ff]	1.31	85.4	91.9	85.9	127.7
$[Cu(bipy)_2I]I$ [gg]	1.31	89	122	92	124
$[Cu(bipy)_2Cl]Cl\cdot 6H_2O$ [hh]	1.28	90.9	118.6	90.9	118.7
$[Cu(bipy)_2(NH_3)][BF_4]_2$ [ii]	1.28	91.6	122.3	92.7	129.5
$[Cu(bipy)_2\{SC(NH_2)_2\}][ClO_4]_2$ [jj]	1.28	92.3	124.4	93.4	
$[Cu\{(C_5H_4N)_2NH\}_2I]I[ClO_4]$ [kk]	1.41	87.3	124.7	87.8	135.5
	1.36	88.0	137.9	88.4	119.8
$[Cu(phen)_2(OH_2)][NO_3]_2$ [ll]	1.33	85.5	110.0	85.5	110.0
$[Cu(phen)_2(OH_2)][BF_4]_2$ [mm]	1.32	86.4	111.7	86.4	111.7
$[Cu(phen)_2I]I\cdot S_8$ [nn]	1.29	92.3	125.3	92.3	125.3
$[Cu(phen)_2(CN)][NO_3]\cdot H_2O$ [oo]	1.29	91.8	129.0	93.9	132.4
$[Zn(MeCOCHCOMe)_2(OH_2)]$ [pp]	1.39	97.5	104.9	100.3	104.9
$[Zn(S_2CNEt_2)_2(C_5H_5N)]\cdot 0.5C_6H_6$ [qq]	1.19	93.9	116.8	95.9	116.1
$[Zn(S_2COEt)_2(C_5H_5N)]$ [rr]	1.17	103.8	115.4	103.8	115.4
$[Mo(Ph_2PCH_2CH_2PPh_2)_2(CO)]$ [ss]	1.28	90.4	92.1	95.0	95.0
$[Ru(Ph_2PCH_2CH_2PPh_2)_2(NO)][BPh_4]\cdot Me_2CO$ [tt]	1.30	90.1	126.1	93.1	134.5
$[Ir(Ph_2PCH_2CH_2PPh_2)_2(CNMe)][ClO_4]$ [uu]	1.34	87.2	106.9	89.3	132.7
$[Ir(Ph_2PCH_2CH_2PPh_2)_2(CO)]Cl$ [vv]	1.33	91	109	91	143
$[NEt_4][Cd(S_2COEt)[Cd(S_2COEt)_3]$ [ww]	1.09	111.8	111.9	119.1	112.7

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The stereochemistries of many of the remaining transition-metal complexes are more complicated. A number are distorted away from structures containing a two-fold axis, that is (BMA − BMC) ≠ (BME − BMD). For example, for $[Fe\{S_2CN(CH_2)_4\}_2I]\cdot 0.5I_2$, BMA − BMC = −6.2°, BME − BMD = 3.9°. This distortion is towards the unsymmetrical square pyramid, in which one of the bidentate ligands spans the edge between a basal site and an apical site (Figures 5 and 6), that is, towards the saddle point in Figures 7 and 8.

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