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Solutions of Octacyanometallate Anions

A Possible Case of Fluctional Structure

D. G. BLIGHT and D. L. KEPERT
The University of Western Australia, Nedlands

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Calculation of ligand-ligand repulsion energies shows that there is no potential energy barrier to prevent a metal atom, surrounded by eight equivalent monodentate ligands, changing from dodecahedral to square antiprismatic stereochemistry in solution. Such a change involves a twisting of ligans about the major dodecahedral axis by about 15° in either direction. A continuation of this distortion in the same direction to an alternative dodecahedron and then to an alternative square antiprism also appears possible. These distortions correspond to a continuous movement of ligands about the metal atom, rather than to the usual reciprocatory bending vibrations. The consequences of this hypothesis are examined for the particular case of the octacyanide ions $[M(CN)_8]^{n-}$ (M = Mo, W, Re; $n = 2, 3, 4$).

Nach Rechnungen an Komplexen mit acht gleichwertigen, einzähligen Liganden zeigt sich, daß es in Lösung zwischen dodekaedrischer und quadratisch-antiprismatischer Konformation keine Potentialschwelle gibt. Solch ein Übergang bedingt eine Verdrehung der Liganden um die Hauptachse des Dodekaeders um ~15°. Auch der weitere Übergang zu einem anderen Dodekaeder bzw. einem anderen quadratischen Antiprisma erscheint möglich. Diese Verzerrung stimmt eher mit einer kontinuierlichen Bewegung der Liganden um das Metallatom, als mit der normalen Knickschwingung überein. Für den Fall der Octacyanoanionen $[M(CN)_8]^{n-}$ (M = Mo, W, Re; $n = 2, 3, 4$) wird diese Hypothese überprüft.

Le calcul des énergies de répulsion électrostatique ligand-ligand montre qu'il n'y a pas de barrière de potentiel pour empêcher un atome métallique, entouré de huit ligands monodentés identiques, de passer en solution, d'une conformation dodécaédrique à une conformation antiprismatique carrée. Une telle modification implique une torsion des ligands d'environ 15° de part et d'autre de l'axe dodécaédrique principal. Cette distorsion peut aussi se prolonger dans la même direction vers un autre dodécaèdre ou un autre antiprisme carré. Ces distorsions correspondent à un mouvement continu des ligands autour de l'atome métallique, plutôt qu'aux vibrations habituelles de déformations réciproques. Les conséquences de cette hypothèse sont examinées pour le cas particulier des ions octocyanures $[M(CN)_8]^{n-}$ (M = Mo, W, Re; $n = 2, 3, 4$).

Introduction

The stereochemistry of the eight coordinate ion $[Mo(CN)_8]^{4-}$ is dodecahedral in crystalline $K_4[Mo(CN)_8] \cdot 2H_2O$ [1, 2], but the structure of the anion in aqueous solution is unknown. The two most obvious possibilities for the structure are the dodecahedron and the square antiprism, since these are the structures commonly found in the solid state for eight coordinate compounds [3, 4, 5, 6] and since they are the two stereochemistries most energetically favourable from considerations of the ligand-ligand repulsion energy [2, 4, 7, 8], covalent bonding [9, 10] or crystal field stabilisation energy [8]. The docecahedron has two types of ligand positions. The four "A" atoms form a tetrahedron which is elongated about the four-fold inversion axis, and the four "B" atoms lie between the pairs of "A" atoms, and form a flattened tetrahedron about the same axis. All ligand positions in a square antiprism are equivalent and are distributed about an eightfold inversion axis.

It is commonly assumed (for example, see [5, 6]) that there exists a potential energy barrier between these two stereochemistries. In this Paper we calculate the ligand-ligand repulsion energies as isolated dodecahedra are distorted to isolated square antiprisms, and show that there is no potential energy barrier to hinder such distortions, at least for this energy term. It is realised that this is not the only relevant factor as other energy terms such as crystal field stabilisation energy, covalent σ-bonding, π-bonding, and solvation should also be considered. The crystal field stabilisation energy for a dodecahedron is the same as that for the square antiprism, and it does not alter as one of the dodecahedral angles is increased while the other is decreased [8], which is partly the distortion required to convert a dodecahedron into a square antiprism. Similarly [9, 10] the bond strength arising from the d^4sp^3 hybridisation required for the dodecahedron is equal to that arising from the d^4sp^3 hybridisation required for the square antiprism. The extent of π-bonding in these complexes has been discussed [5, 11, 12], but it is difficult to assess the actual energy difference. Finally it is not possible to predict the solvation energies, but the difference is not expected to be large. The analogous lattice energy in the solid state appears crucially important in deciding the stereochemistry, as attempts to correlate the preferred stereochemistry with other factors have not been very successful [3, 4, 5, 6].

Results

The dodecahedron and square antiprism are both particular examples of the more general stereochemistry shown in Fig. 1. The points on the surface of the sphere are divided into two sets of four as defined by Fig. 1. The four points

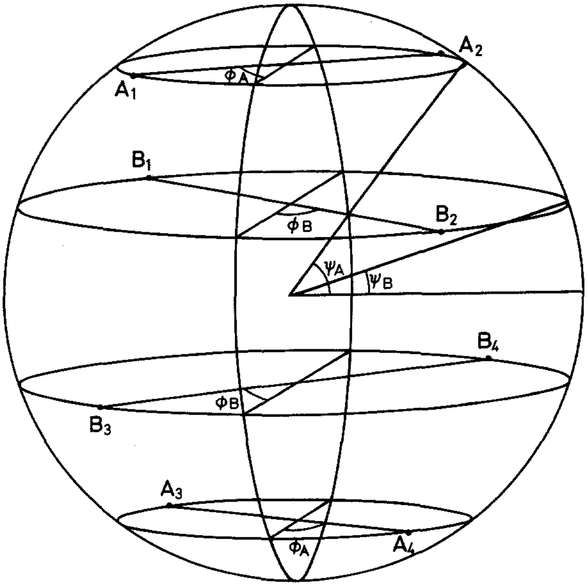

Fig. 1. Generalised eight coordinate stereochemistry. The "A" points have "longitude" ϕ_A and "latitude" ψ_A. The "B" points have "longitude" ϕ_B and "latitude" ψ_B

marked "A" are defined by two independent variables, their "longitude" ϕ_A and "latitude" ψ_A, and the four points marked "B" are similarly defined by their "longitude" ϕ_B and "latitude" ψ_B. The ligand-ligand distances in terms of the radius of the sphere, r, are given in Table 1.

Table 1

$A_1A_2 = A_3A_4 = 2r\cos\psi_A$
$A_1A_3 = A_2A_4 = [4r^2\sin^2\psi_A + 4r^2\cos^2\psi_A\cos^2\phi_A]^{\frac{1}{2}}$
$A_1A_4 = A_2A_3 = [4r^2\sin^2\psi_A + 4r^2\cos^2\psi_A\sin^2\phi_A]^{\frac{1}{2}}$
$A_1B_1 = A_2B_2 = A_3B_3 = A_4B_4 = [2r^2 - 2r^2\sin\psi_A\sin\psi_B + 2r^2\cos\psi_A\cos\psi_B\cos(\phi_A + \phi_B)]^{\frac{1}{2}}$
$A_1B_2 = A_2B_1 = A_3B_4 = A_4B_3 = [2r^2 - 2r^2\sin\psi_A\sin\psi_B - 2r^2\cos\psi_A\cos\psi_B\cos(\phi_A + \phi_B)]^{\frac{1}{2}}$
$A_1B_3 = A_2B_4 = A_3B_1 = A_4B_2 = [2r^2 + 2r^2\sin\psi_A\sin\psi_B - 2r^2\cos\psi_A\cos\psi_B\cos(\phi_A - \phi_B)]^{\frac{1}{2}}$
$A_1B_4 = A_2B_3 = A_3B_2 = A_4B_1 = [2r^2 + 2r^2\sin\psi_A\sin\psi_B + 2r^2\cos\psi_A\cos\psi_B\cos(\phi_A - \phi_B)]^{\frac{1}{2}}$
$B_1B_2 = B_3B_4 = 2r\cos\psi_B$
$B_1B_3 = B_2B_4 = [4r^2\sin^2\psi_B + 4r^2\cos^2\psi_B\cos^2\phi_B]^{\frac{1}{2}}$
$B_1B_4 = B_2B_3 = [4r^2\sin^2\psi_B + 4r^2\cos^2\psi_B\sin^2\phi_B]^{\frac{1}{2}}$

The total ligand-ligand repulsion energy U is obtained by summing over the 28 individual ligand-ligand repulsion terms and expressing the result in the form

$$U = \sum_{ij} u_{ij} = X\frac{Z^2e^2}{r} + Y\frac{be^2}{r^n}$$

where Z^2e^2 is the product of the charges and b is a constant. The numerical coefficient X measures the Coulombic repulsion and the numerical coefficient Y measures the Born repulsion arising from the repulsion of the outer electrons of the atoms. The Born exponent n is taken to lie between the limits of 6 and 12. For polarisable ions a third term involving the dispersion energy should be included in the above equation, but the effect of this term will not be discussed separately, as it is of the same form as the Born term for $n = 6$.

The coefficients X and Y were calculated as a function of all four variables, ϕ_A, ψ_A, ϕ_B and ψ_B, with the additional condition that $\psi_A \overset{=}{>} \psi_B$. The results are shown as a function of ϕ_A and ϕ_B in the form of a potential energy surface in Fig. 2 for $n = 1$ (the Coulombic interaction). The diagrams for $n = 6$ and 12 are very similar. The energies have been normalised so that the bottom of the potential energy wells corresponding to the square antiprism are unity. The energy for each set of values of ϕ_A and ϕ_B was obtained by allowing ψ_A and ψ_B to systematically vary until a minimum was obtained.

This three dimensional energy surface for any given pair of values of ϕ_A and ϕ_B is similar to that given in a previous Paper [4] for the particular case of the dodecahedron. It should be noted that the angular parameters used in the earlier paper are related to those in this work by $\theta_A = 90 - \psi_A$ and $\theta_B = 90 - \psi_B$ where θ_A and θ_B are the angles made to the four-fold inversion axis.

Fig. 2 represents the projection of the valleys in the *five* dimensional potential energy surface onto the $\phi_A - \phi_B$ plane. If the condition $\psi_A \overset{=}{>} \psi_B$ is not used the potential energy surface is reflected about the axes joining ($\phi_A = 0$, $\phi_B = 90$) and ($\phi_A = 90$, $\phi_B = 0$), due merely to an interchange of the "A" and "B" labels on the atoms. This has no chemical significance and may cause confusion, particularly towards the centre of the potential energy diagram. For values near ($\phi_A \sim 20$, $\phi_B \sim 80$), the potential energy surface has no minimum for $\psi_A \overset{=}{>} \psi_B$, and this section of the diagram is therefore left blank. The potential energy surface is symmetrical about the dodecahedron ($\phi_A = \phi_B = 45°$), since the A_1A_2 atoms can be twisted away from 90° relative to the A_3A_4 atoms in either a clockwise or anticlockwise direction.

Distortion of the dodecahedron (D) with ($\phi_A = \phi_B = 45°$) by decreasing ϕ_A and increasing ϕ_B along the "reaction coordinate" (Fig. 2) produces the first square antiprism (A) at ($\phi_A \sim 30°$, $\phi_B \sim 55°$). A further continuation along the "reaction coordinate" generates an alternative dodecahedron (D′) at ($\phi_A \sim 26°$, $\phi_B \sim 62°$) which can then be transformed into an alternative second square antiprism (A′) at ($\phi_A = 22.5°$, $\phi_B = 67.5°$). A continuation up this potential valley to ($\phi_A = 0°$, $\phi_B = 90°$) leads to a cube (C). Movement up a different potential valley from the first square antiprism forms another cube (C′) at ($\phi_A = 0°$, $\psi_A = 54.7°$, $\phi_B = 54.7°$, $\psi_B = 0°$). A fifth cube can be generated on the five dimensional potential energy surface by keeping $\phi_A = \phi_B = 45°$, and decreasing ψ_A and increasing ψ_B so that $\psi_A = \psi_B = 35.3°$.

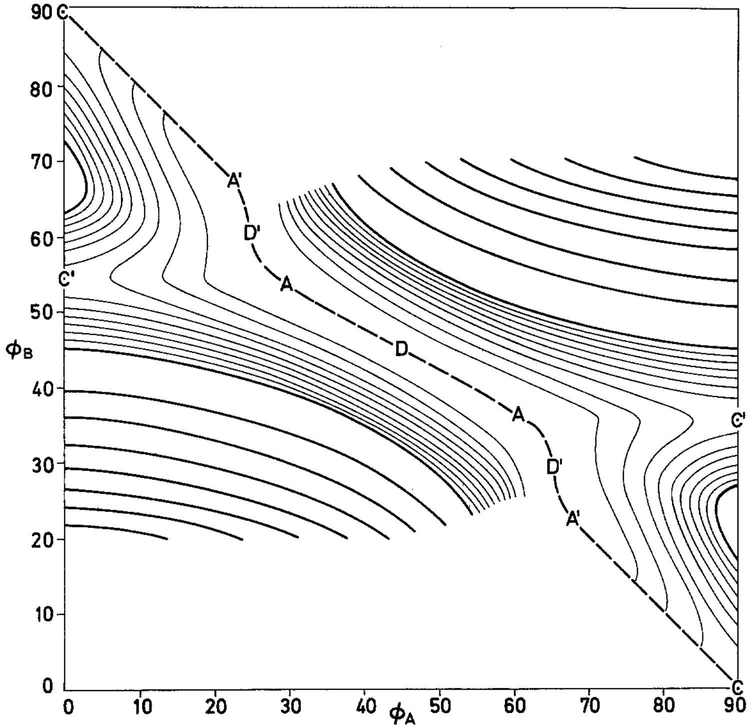

Fig. 2. Projection of the valleys in the five dimensional potential energy surface for the Coulombic term onto the $\phi_A - \phi_B$ plane. The faint contour lines are for 0.1 % energy increases and the dark contour lines for 1 % energy increases above the bottom of the potential energy surface corresponding to the square antiprism. The "reaction coordinate" is shown by the broken line. The positions of the regular stereochemistries are shown by D (for dodecahedron), A (for square antiprism), and C (for cube)

The potential energy profiles along the "reaction coordinates" are shown in Fig. 3. The precise values of the angles ϕ_A, ψ_A, ϕ_B and ψ_B, and of the numerical coefficients X and Y for these regular stereochemistries are given in Tab. 2.

Discussion

Figs. 2 and 3 show that there is no potential energy barrier between the dodecahedron, for which $\phi_A = \phi_B = 45°$, *and the square antiprism which occurs*

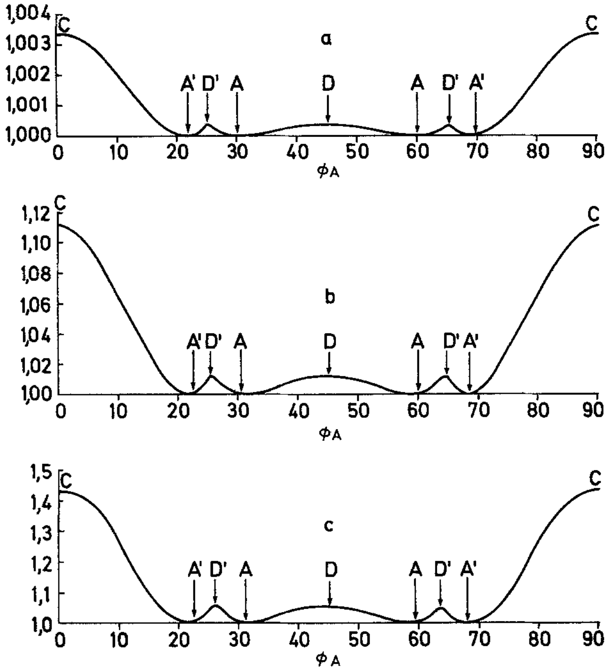

Fig. 3 a—c. Relative ligand-ligand repulsion energies along the "reaction coordinates" for: a Coulombic term ($n = 1$), b Born term ($n = 6$), c Born term ($n = 12$)

Table 2

	Dodecahedron 1			Square Antiprism 1			Dodecahedron 2			Square Antiprism 2			Cube		
	Coulombic Term	Born Term $n=6$	Born Term $n=12$	Coulombic Term	Born Term $n=6$	Born Term $n=12$	Coulombic Term	Born Term $n=6$	Born Term $n=12$	Coulombic Term	Born Term $n=6$	Born Term $n=12$	Coulombic Term	Born Term $n=6$	Born Term $n=12$
ϕ_A	45.0	45.0	45.0	29.5	30.9	31.4	24.9	25.5	26.2	22.5	22.5	22.5	0	0	0
ϕ_B	45.0	45.0	45.0	53.8	55.3	55.9	60.7	61.7	61.9	67.5	67.5	67.5	90	90	90
ψ_A	51.6	52.7	52.9	49.9	51.1	51.5	42.2	42.1	41.9	34.1	32.9	32.1	35.3	35.3	35.3
ψ_B	18.2	18.6	19.2	18.5	18.8	18.9	25.9	25.4	25.2	34.1	32.9	32.1	35.3	35.3	35.3
Numerical Coefficient X or Y	19.682	5.245	1.592	19.675	5.185	1.503	19.682	5.245	1.592	19.675	5.185	1.503	19.741	5.758	2.170

at $\phi_A \sim 30^\circ$ *and* $\phi_B \sim 55^\circ$. Such a result cannot readily be predicted from models, and may be unexpected by comparison with the much more rigid tetrahedral and octahedral stereochemistries which are more commonly encountered in chemistry.

It is important to emphasise that all eight positions of a square antiprism are identical, and that any one of the four two-fold rotation axes may be chosen to become the principal four-fold inversion axis of the dodecahedron. Thus movement along the "reaction coordinate" between the first square antiprism and the dodecahedron necessarily removes the uniqueness of the "A" and "B" atoms of the dodecahedron.

The dodecahedron sits on a slight saddle between two square antiprisms in the potential energy surface. It is not possible to quantitatively convert this difference in the ligand-ligand repulsion coefficients into actual energy units, but it is certainly within the limits 0.1—1 kcal/mol (or 30—300 cm^{-1}) [2, 4, 8]. This difference is less than uncertainties present in estimates of covalent bonding, crystal field stabilisation energy, π-bonding and solvation. It may even be possible that this distortion, which involves changing the angular parameters by about 30°, may occur in the ground vibrational state.

Figs. 2 and 3 also show that additional movement along the "reaction coordinate" to ($\phi_A = 17°$, $\psi_A = 33°$) is equally possible, that is an overall change in the angular parameters of the "A" atoms by 33° from the dodecahedron, or by 66° while moving in the energy trough between the two extreme square antiprisms. The term "vibration" should not be used for such movements, as the axes which define the atoms as "A" or "B" can be changed each time a square antiprismatic or dodecahedral stereochemistry is traversed, so the movement of ligands on the surface of the sphere may be visualised as continuous rather than the usual reciprocatory bending vibration.

The Octacyano-Metallate Anions

The hypothesis of a fluctional structure is more consistent with the experimental data on solutions of $[Mo(CN)_8]^{4-}$, than either a rigid dodecahedron or a rigid square antiprism. The structures of $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$, $[W(CN)_8]^{3-}$, $[Re(CN)_8]^{3-}$ and $[Re(CN)_8]^{2-}$ appear similar to $[Mo(CN)_8]^{4-}$ [13, 14, 15]. The Raman spectrum of $[Mo(CN)_8]^{4-}$ in aqueous solution in conjunction with an early imprecise infra red spectrum of solid $K_4[Mo(CN)_8] \cdot 2H_2O$ has been interpreted in terms of a square antiprismatic structure [16], but this conclusion may be qualified by the photolytic decomposition of this ion [17] to CN^- and $[MoO_2(CN)_4]^{4-}$ [18]. The most recent work [19] on the infra red spectrum of solid $K_4[Mo(CN)_8] \cdot 2H_2O$ shows a more complex spectrum with at least six bands in the $C \equiv N$ stretching region between 2100 and 2140 cm^{-1}, whereas in solution only a single broad band covering the entire region is observed as expected for a fluctional structure; it is significant that the spectrum could not be resolved by varying the solvent (water, ethanol, water-glycerol, saturated aqueous KBr), or by freezing or cooling the solutions to −60°. The *esr* spectra of $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ in aqueous solution are also the same at room temperature as in frozen water-glycerine mixtures at liquid nitrogen temperatures [11, 20]. The ^{13}C-*nmr* spectrum of aqueous solutions of $[Mo(CN)_8]^{4-}$ shows that all carbon atoms appear equivalent [21], which is again consistent with a structure which is non-rigid on an *nmr* time scale. The visible and ultraviolet spectrum of aqueous $[Mo(CN)_8]^{4-}$ cannot be used as evidence to favour any particular structure [13, 14, 22].

If a small potential energy barrier did exist between the dodecahedron and the square antiprism, it would be expected that both rigid stereochemistries would exist in thermodynamic equilibrium, the relative concentrations of the two species being dependent upon experimental conditions. We have examined in detail the ultra violet and visible spectrum of aqueous $[Mo(CN)_8]^{4-}$ as a function of temperature (0—80°) and cation present, and could detect no change, even under conditions where the anion must have been completely ion paired, for example in a solution saturated with magnesium chloride.

Under such conditions of non-rigidity, it may be misleading to designate the structure with point symmetry groups assuming a rigid structure. Thus if the major four-fold rotation-reflection axis (S_4) of the dodecahedron is defined as the z-axis, the most stable atomic orbital becomes the $d_{x^2-y^2}$ [8, 14, 23] or d_{xy} [24] depending upon the choice of minor axes. If the dodecahedron is now distorted to a square antiprism by twisting about the S_4 axis as described in this paper, this axis becomes one of the minor C_2 rotation axes of the square antiprism, and one of the C_2 rotation axes of the dodecahedron becomes the eightfold rotation-reflection axis (S_8) of the square antiprism. If this major S_8 axis is now defined as the z-axis, the most stable atomic orbital becomes the d_{z^2} [8, 25]. It is important to emphasise that both spatially and energetically, this d_{z^2} orbital of the rigid square antiprism is equivalent to the $d_{x^2-y^2}$ (or d_{xy}) orbital of the rigid dodecahedron, the difference in labelling arising simply from a different choice of axes.

The symmetry of molecules which have no rigid stereochemistry have been discussed in terms of a Schrödinger supergroup **S** [26], while bullvalene, which in many respects resembles these octacyanides, has been described as of fluctional structure [27].

Experimental. All calculations were carried out on the University of Western Australia's PDP-6 computer.

Standard techniques [28] were used to prepare $K_4[Mo(CN)_8]\,2H_2O$, and solutions of other salts were obtained by cation exchange.

The spectra were measured using a Unicam S.P. 700 spectrophotometer.

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Dr. D. L. Kepert
The University of Western Australia
Chemistry Department
Nedlands Western Australia