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Chemical Reaction Coordinates from Crystal Structure Data. I

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A detailed model for the structural pathway of the ligand-exchange reaction $XCdL_3 + Y \rightarrow X\cdots CdL_3\cdots Y \rightarrow X + L_3CdY$ is obtained from X-ray structural data of 11 five-coordinate cadmium complexes. The complexes show distorted trigonal-bipyramidal coordination with three equatorial sulfur ligands (L) and iodide, sulfur, or alcoholic oxygen (X, Y) in axial positions. The axial distances are brought to a common basis by subtracting from them the corresponding sum of covalent radii to obtain distance increments Δx and Δy. The main trends observed in these increments are as follows: small increments Δx are accompanied by large increments Δy and by large deviations Δz of cadmium out of the plane of the three equatorial sulfurs toward ligand X; with increasing increment Δx both Δy and Δz become smaller; if Δx equals Δy, then Δz is zero, corresponding to trigonal-bipyramidal coordination of cadmium. These correlations of Δx, Δy, and Δz obtained from a sequence of static pictures (crystal structures) are interpreted in terms of the structural changes (reaction coordinate) occurring in the course of a nucleophilic displacement reaction at tetrahedrally coordinated cadmium with a trigonal-bipyramidal activated complex or intermediate. An alternative representation of the experimental data in terms of the symmetry coordinates of a trigonal bipyramid is given. It is shown that information may be obtained, at least in principle, about the relative magnitude of potential constants describing the potential energy surface of the displacement reaction.

Introduction

The energetic and kinetic aspects of chemical reactions have been investigated extensively by experiment. Mechanistic interpretations of the data often imply a sequence of not very precisely defined but continuous structural changes along the reaction coordinate. These changes are usually not accessible to direct experimental investigation, in particular in the region of the transition state of reactions with high activation energies. For some of the faster ligand-exchange reactions at metal ions occurring with low activation energy it is possible, at least in principle, to freeze out the reacting particles into a crystal lattice at any point along the reaction coordinate by suitable chemical perturbations, *e.g.*, crystal packing forces.

In practice, however, it is very difficult to vary such perturbations in a systematic way in order to sample a representative number of points along the reaction coordinate. There is another approach to this problem, namely, to try to derive the detailed structural pathway for a particular type of reaction by searching for certain kinds of correlations in a set of selected structural data obtained from crystal structure studies.

As an example we consider here the observed structural parameters for 11 different arrangements of ligands about cadmium atoms.[1-4] These arrangements can all be regarded as trigonal bipyramids with three equatorial sulfurs and various axial ligands. Even a casual inspection of the data reveals a correlation between the axial bond lengths and the nonplanarity of the CdS_3 fragment. If we take the view that these arrangements represent a sequence of frozen-in points along the reaction coordinate of the substitution reaction

$$XCdS_3 + Y \rightarrow X\cdots CdS_3\cdots Y \rightarrow X + S_3CdY \qquad (1)$$

then analysis of the structural data should yield details of the sequence of structural changes that occur in the course of this reaction.

Selection and Treatment of Data

The data are taken from four crystal structure analyses: the compound $Cd_5(SCH_2CH_2OH)_8 \cdot SO_4 \cdot H_2O$ forms decanuclear cations containing four-, five-, and six-coordinated cadmium atoms.[1] The structure of $Cd(SCH_2CH_2OH)_2$ consists of infinite two-dimensional layers with four- and five-coordinated cadmium atoms.[2] The building block of $Cd_2(SCH_2CH_2OH)_3I$ is polynuclear, consisting of eight cadmiums at the corners of a cube with an iodine atom at the center; the cadmium atoms show four-, five-, and sixfold coordination.[3] The structure of $Cd\{(CH_3CH_2CH_2O)_2PS_2\}_2$ consists of discrete dimeric units.[4]

Cadmium atoms showing five-coordination or four-coordination with a fifth ligand above a triangular face were selected from these structures to give eleven cases all containing three sulfurs as equatorial ligands. The relevant interatomic distances and angles are given in Table I. The Cd–S bond lengths all lie in the range 2.47–2.60 Å with a mean value 2.52 Å (cadmium sulfide, 2.52 Å[5]). They can be regarded as practically constant throughout. The equatorial bond angles deviate from threefold symmetry with no apparent regularity. In all cases the cadmium atom is displaced from the plane defined by the three equatorial sulfurs. The displacements Δz are given in Table II. The axial ligand toward which Cd is displaced we call ligand X; the other, ligand Y. The axial ligands are as follows: both iodine (five cases), both sulfur (one case), sulfur and oxygen (three cases), iodine and oxygen (two cases). In order to bring the axial distances to a common basis we subtract from them the corresponding sums of covalent radii, taken as 1.48 Å (Cd), 1.28 Å (I), 1.04 Å (S), and 0.66 Å (O),[6] to obtain the corresponding increments Δx and Δy. In all cases the observed axial distances are greater than the sums of the respective covalent radii. The increments Δx and Δy are therefore all positive and represent the deviation from the closest possible distance between Cd and X or Y (Table II and Figure 1).

Correlations

A suggestive way of looking at the results is shown in Figure 2 where Δx and Δy, the increments in the two axial distances from normal bond distances, are plotted against

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[1] P. Strickler, *Chem. Commun.*, 655 (1969); unpublished results.

[2] H. B. Burgi, submitted for publication in *Helv. Chim. Acta.*

[3] H. B. Burgi, H. Gehrer, P. Strickler, and F. Winkler, work in preparation.

[4] S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 8, 2410 (1969).

[5] For references see R. W. G. Wyckoff, "Crystal Structures," Vol. I, Interscience, New York, N. Y., 1963, p 110, 112, 188.

[6] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 224, 246, 514.

Table I. Internal Coordinates of the Trigonal-Bipyramidal $XCdS_3Y$ Complexes[a]

X	Y	d_1	d_2	d_3	d_X	d_Y	α_{12}	α_{23}	α_{31}	α_{1X}	α_{2X}	α_{3X}	α_{1Y}	α_{2Y}	α_{3Y}	α_{XY}
I	I	2.52	2.56	2.58	2.81	3.80	109	115	117	104	105	105	75	72	78	176
I	I	2.50	2.50	2.53	2.86	3.68	108	115	120	108	103	100	68	82	79	174
I	I	2.50	2.53	2.54	2.89	3.67	128	113	106	106	100	99	69	84	81	175
I	I	2.50	2.51	2.53	2.92	3.50	122	113	113	102	99	103	85	77	72	172
I	I	2.51	2.52	2.52	2.93	3.50	108	121	117	104	101	102	71	83	78	175
S	S	2.49	2.50	2.55	2.59	3.19	122	115	116	107	109	79	70	86	86	162
S	O	2.52	2.54	2.56	2.69	2.62	126	116	115	100	94	92	90	75	88	169
I	O	2.52	2.52	2.56	3.08	2.47	125	116	118	94	90	92	75	88	101	166
I	O	2.47	2.52	2.55	3.17	2.48	125	113	121	91	93	95	87	76	98	165
O	S	2.50	2.50	2.56	2.41	2.84	112	130	118	99	98	77	97	83	89	163
O	S	2.49	2.50	2.60	2.42	2.87	133	113	114	99	75	104	89	87	88	161

[a] See Figure 1 for meaning of symbols. Distances are given in angstroms; angles, in degrees. Estimated standard deviations from the X-ray crystal structure analyses are $\sigma(\text{Cd–I}) \leqslant 0.01$ Å, $\sigma(\text{Cd–S}) \leqslant 0.02$ Å, $\sigma(\text{Cd–O}) \leqslant 0.05$ Å, $\sigma(\alpha_{\text{ICdI}}) \leqslant 0.3°$, $\sigma(\alpha_{\text{ICdS}}) \leqslant 0.6°$, $\sigma(\alpha_{\text{ICdO}}) \leqslant 1.3°$, $\sigma(\alpha_{\text{SCdS}}) \leqslant 0.8°$, $\sigma(\alpha_{\text{SCdO}}) \leqslant 1.4°$.

Table II. Deviations Δz of Cd from the Plane Defined by S_1, S_2, and S_3, Distance Increments Δx and Δy, and Numerical Values of the Symmetry Displacement Coordinates S_2, S_3, S_4, S_6, S_7, and S_8[a]

X	Y	Δz	Δx	Δy	S_2	S_3	S_4	S_6	S_7	S_8
S		0.84	0.00				48	0	0	0
I	I	0.66	0.05	1.04	0.77	0.70	36	6	3	3
I	I	0.59	0.10	0.92	0.72	0.58	33	9	5	11
I	I	0.52	0.13	0.91	0.74	0.55	29	16	5	12
I	I	0.51	0.16	0.74	0.64	0.41	29	7	7	7
I	I	0.55	0.17	0.74	0.64	0.40	31	9	5	8
S	S	0.41	0.07	0.64	0.50	0.40	22	5	15	22
S	O	0.25	0.17	0.48	0.46	0.22	13	9	11	8
I	O	0.10	0.32	0.33	0.46	0.01	5	7	12	14
I	O	0.13	0.41	0.34	0.53	−0.05	7	9	12	10
O	S	0.04	0.27	0.32	0.42	0.04	2	13	15	14
O	S	0.08	0.28	0.35	0.45	0.05	6	16	16	15

[a] Δz, Δx, Δy, S_2, and S_3 are given in angstroms; S_4, S_6, S_7, and S_8, in degrees.

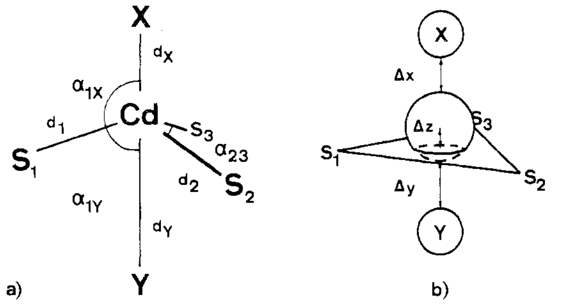

Figure 1. (a) Angles and distances in a distorted trigonal-bipyramidal cadmium complex. (b) Distance increments Δx, Δy, and Δz. The diameters of the atoms indicate covalent radii.

Δz, the displacements of the Cd atom from the equatorial plane toward ligand X.

To the eleven sets of observed points we can add a twelfth with $\Delta x = 0$ Å, $\Delta y = \infty$ Å, $\Delta z = 0.84$ Å, corresponding to the geometry of an ideal CdS_4 tetrahedron plus an infinitely distant S atom. It is quite clear from Figure 2 that the approach of ligand Y toward the Cd atom is associated with a gradual flattening of the CdS_3 pyramid and with a concomitant increase in the Cd-X distance from its normal bond distance. For $\Delta x = \Delta y \approx 0.32$ Å, $\Delta z = 0$ Å (*i.e.*, the CdS_3 unit is coplanar) and the complex $XCdS_3Y$ is trigonal bipyramidal. Note that in the course of passing from tetrahedron to trigonal bipyramid the change in Δx (~0.3 Å) is much less than the change in Δz (0.84 Å).

If the Δy-Δz plot is reflected across the line $\Delta z = 0$ as in Figure 3, it is clear that Δx and Δy can be treated as a single function of Δz, where

$$\Delta x = g(\Delta z); \quad \Delta y = g(-\Delta z) \tag{2}$$

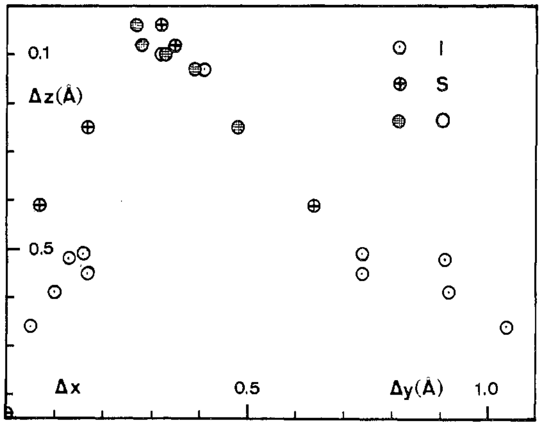

Figure 2. Correlation of Δz with pairs of distance increments Δx and Δy (Table II).

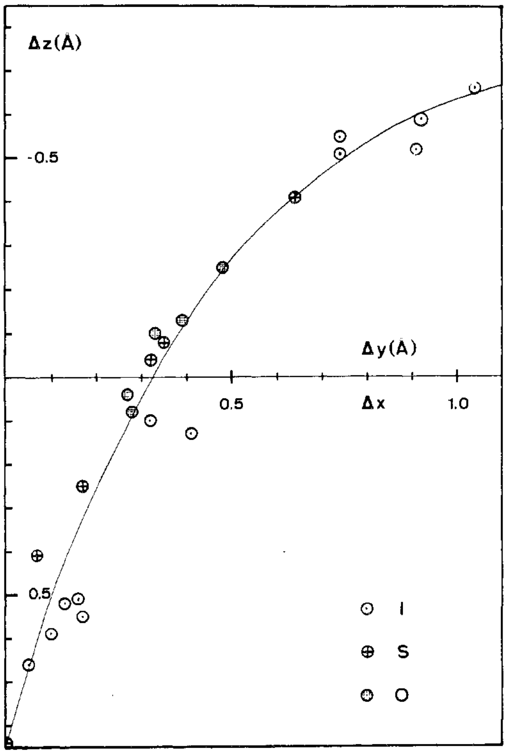

Figure 3. Plot of the distance increments Δx and Δy as a single function of Δz.

The experimental data have been fitted to a logarithmic curve described by the equation

$$\Delta x, \Delta y = g(\pm\Delta z) = a \log(\pm\Delta z + \Delta z_{\max}) + b \tag{3}$$

For $\Delta z_{\max}$ the value of an ideal CdS_4 tetrahedron, 0.84 Å, was assumed. If it is required that the curve passes through the points $\Delta z = -0.84$ Å, $\Delta y = \infty$ Å and $\Delta z = 0.84$ Å, $\Delta x = 0.00$ Å, then b_1 equals 0.23 Å. The only variable left is a_1, which was determined by a least-squares calculation to be -1.05 Å. Adjusting both a and b by least squares results in $a_2 = -1.02$ Å and $b_2 = 0.25$ Å in good agreement with a_1 and b_1 (the smooth curves in the figures are based on a_1 and b_1).

Figure 4 shows how the axial distance increments Δx and Δy are correlated with each other. The smooth curve corresponds to pairs of Δx and Δy obtained from eq 3. The interpretation of these correlations in terms of the detailed geometrical pathway of the ligand-exchange reaction $Y + CdS_3X \rightarrow Y\cdot\cdot\cdot CdS_3\cdot\cdot\cdot X \rightarrow YCdS_3 + X$ is clear. The reaction starts with the tetrahedral CdS_3X molecule with a fifth ligand Y on the tetrahedral face opposite X. As the ligand Y approaches Cd, the CdS_3 pyramid flattens and X moves gradually away from Cd. At equal distances $Cd\cdot\cdot\cdot X$ and $Cd\cdot\cdot\cdot Y$ the four atoms of the CdS_3 unit are coplanar. As Y comes still closer to Cd, X moves away further, and the reaction ends with $YCdS_3$ and dissociated X. The same general kind of pathway has been postulated for S_N2 mechanisms in organic reactions[7] but its detailed geometry has so far eluded experimental investigation.

However, LCAO-MO-SCF *ab initio* calculations[8,9] on HCH_3H^- and FCH_3F^- have yielded results that are similar to ours. Both calculations lead to very small lengthening of the equatorial C-H bonds (Δ(C-H) = 0.06 Å in HCH_3H^- and 0.02 Å in FCH_3F^-) in the trigonal-bipyramidal arrangement. No clear change can be detected for the CdS_{eq} distances from our data. Both calculations predict that the axial bonds in the trigonal-bipyramidal arrangement are substantially longer than the corresponding bonds in the tetrahedral educt and product molecules ($\Delta(C\cdot\cdot\cdot X) = 0.68$ Å for HCH_3H^- and 0.46 Å for FCH_3F^-). Apart from our result, the only experimental value available for comparison is for the system $I_2 + I^-$, where the bond length in I_3^- is 0.23 Å longer than in I_2.[10] (The correlation between the two bond lengths observed for I_3^- in various crystal environments is very similar to the one found for the $XCdS_3Y$ system, but the presence of equatorial lone pairs rather than equatorial ligands prevents a more detailed comparison.) The average lengthening found in the $XCdS_3Y$ complexes is 0.32 Å. This is equal to the average $\langle \Delta R \rangle$ of the differences between ionic and covalent radii for all pairs $Cd\cdot\cdot\cdot X$ and $Cd\cdot\cdot\cdot Y$, defined as

$$\langle \Delta R \rangle = \frac{1}{22}\sum_{i=1}^{11}[2r_{\text{ionic}}(\text{Cd}) + r_{\text{ionic}}(X_i) + r_{\text{ionic}}(Y_i) - 2r_{\text{cov}}(\text{Cd}) - r_{\text{cov}}(X_i) - r_{\text{cov}}(Y_i)] \qquad (4)$$

The ionic radii are taken as 0.97 Å (Cd^{2+}), 2.16 Å (I^-), 1.84 Å (S^{2-}), and 1.40 Å (O^{2-}).[6] There is just a hint from Figure 3 that for $\Delta z = 0$ the bond lengthening Δx depends on the nature of the ligand X with $\Delta x(\text{Cd-O}) < \Delta x(\text{Cd-S}) < \Delta x(\text{Cd-I})$. The corresponding values of ΔR are +0.23, +0.29, and +0.37 Å for O, S, and I, respectively.

One is tempted to conclude that the bonding to the axial substituents in the trigonal bipyramid is mainly *ionic* since the main contribution to covalent bonding would have to come from a molecular orbital involving the high-lying 5p orbital of Cd and the lower lying antisymmetric linear combination of the two ligand σ orbitals, an interaction which is not expected to be very strong. The *ab initio* calculations on HCH_3H^- and FCH_3F^- show[8,9] that on forming the trigonal-bipyramidal complexes charge is pulled away from the equatorial hydrogen atoms and from the carbon atom into the axial substituents. The Mulliken population analysis of the wave functions gives charges of 0.131+ on each of the hydrogen atoms of CH_4 and of 0.391− on the fluorine atoms of FCH_3 but of 0.613− on the axial hydrogen atoms of HCH_3H^- and 0.769− on the axial fluorine atoms in FCH_3F^- and thus hints at a large ionic contribution to the interaction between central atom and axial substituents in these bipyramidal ions. It is well known that the most electronegative substituents tend to occupy the axial positions in a trigonal-bipyramidal molecule.[11] A detailed MO study of pentacoordinate phosphorus is in agreement with this tendency and also shows a buildup of negative charge in the axial substituents at the expense of the equatorial substituents and the central phosphorus atom.[12,13]

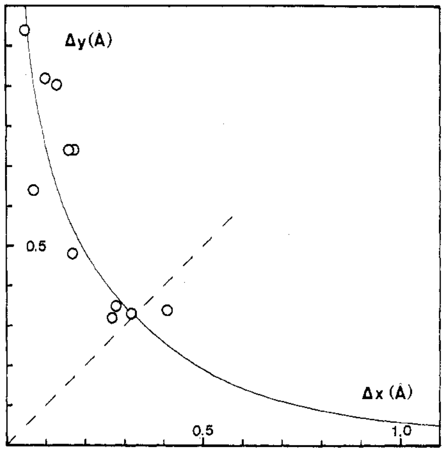

Figure 4. Correlation of the axial distance increment Δx with increment Δy.

The similarities among the different reactions $HCH_3 + H^-$, $FCH_3 + F^-$, $I_2 + I^-$, and $XCdS_3 + Y$ are astonishing and unexplained. In any case, they provide a justification for merging our structural data involving different axial ligands (I, S, O) into one data set; the differences among the various Cd complexes with respect to substitution reactions are certainly not expected to be larger than those among the other reactions.

The analytical form of eq 3 was inspired by Pauling's formula relating changes in interatomic distance Δd to bond numbers n[14]

$$\Delta d = C \log n \qquad 0 < n < 1 \qquad (5)$$

Indeed a simple transformation of eq 3 leads to

$$\Delta x,\ \Delta y = g(\pm\Delta z) = -1.05 \log [(\pm\Delta z + 0.84)/1.68] \qquad (6)$$

$$n_x,\ n_y = (\pm\Delta z + 0.84)/1.68 \qquad \begin{matrix} 0 < n_x < 1 \\ 0 < n_y < 1 \end{matrix} \qquad (7)$$

This implies that for the data considered here the bond number n is linearly dependent on Δz and also that

$$n_x + n_y = 1 \qquad (8)$$

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[7] E. Fischer, *Justus Liebigs Ann. Chem.*, **381**, 123 (1911).

[8] C. D. Ritchie and G. A. Chappell, *J. Amer. Chem. Soc.*, **92**, 1819 (1970).

[9] G. Berthier, D.-J. David, and A. Veillard, *Theor. Chim. Acta*, 14, 329 (1969).

[10] For a compilation of data and references see H. A. Bent, *Chem. Rev.*, **68**, 587 (1968) (in particular, p 602).

[11] For a review see R. J. Gillespie, "Molecular Geometry," Van Nostrand-Reinhold, London, 1972, in particular p 68.

[12] R. Hoffman, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 3047 (1972).

[13] J. P. Lowe, *J. Amer. Chem. Soc.*, 93, 301 (1971).

[14] L. Pauling, *J. Amer. Chem. Soc.*, **69**, 542 (1947).

i.e., the sum of the bond numbers of the axial bonds equals unity at every stage of the reaction. Equation 3 seems to provide a very general and reliable means of correlating interatomic distances with degree of bonding over a wide range of values, provided the numerical constants can be determined. Equation 3 reproduces the trends observed in the interatomic distance data[10] not only of I_3^- but also of the donor-acceptor complexes between a nitrogen lone pair and a carbonyl carbon atom.[15]

Symmetry Coordinates

An alternative representation of the experimental data can be given in terms of internal symmetry displacement coordinates of a trigonal bipyramid[16] (Table II)

$$S_2 = (\Delta y + \Delta x)/\sqrt{2} \qquad (A'_1) \qquad (9)$$

$$S_3 = (\Delta y - \Delta x)/\sqrt{2} \qquad (A''_2) \qquad (10)$$

$$S_4 = (\Delta\alpha_{1X} - \Delta\alpha_{1Y} + \Delta\alpha_{2X} - \Delta\alpha_{2Y} + \Delta\alpha_{3X} - \Delta\alpha_{3Y})/\sqrt{6} \qquad (A''_2) \qquad (11)$$

$$S_{6a} = (2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13})/\sqrt{6} \qquad (E') \qquad (12)$$

$$S_{6b} = (\Delta\alpha_{12} - \Delta\alpha_{13})/\sqrt{2} \qquad (E') \qquad (13)$$

$$S_6 = \sqrt{S_{6a}{}^2 + S_{6b}{}^2} \qquad (14)$$

$$S_{7a} = (2\Delta\alpha_{1X} - \Delta\alpha_{2X} - \Delta\alpha_{3X} + 2\Delta\alpha_{1Y} - \Delta\alpha_{2Y} - \Delta\alpha_{3Y})/\sqrt{12}, \text{ etc.} \qquad (E') \qquad (15)$$

$$S_{8a} = (2\Delta\alpha_{1X} - \Delta\alpha_{2X} - \Delta\alpha_{3X} - 2\Delta\alpha_{1Y} + \Delta\alpha_{2Y} + \Delta\alpha_{3Y})/\sqrt{12}, \text{ etc.} \qquad (E'') \qquad (16)$$

Although the symmetry coordinates are strictly defined only for infinitesimal displacements, they are useful in the present study of finite displacements.

Figure 5 shows a plot of S_4 *vs.* S_3. The smooth curve is obtained from regression 3 and eq 10 and 11 with the help of the trigonometric relationship

$$\alpha_{iX} = \text{arc cos}\,(\Delta z/2.52) \quad (i = 1, 2, 3) \qquad (17)$$

An analogous plot of S_2 and S_3 is given in Figure 6 with the corresponding curve calculated from regression 3 and eq 9 and 10. The two diagrams give an alternative description of reaction 1 which is best discussed in terms of the decay of the trigonal-bipyramidal complex. The decay is initiated by the antisymmetric stretching of the axial bonds with simultaneous out-of-plane bending of the CdS_3 moiety (Figure 5). Initially, the complex does not deform along the symmetric stretch coordinate; as X moves closer to Cd, Y moves away by the same amount. However, as the decay proceeds, the symmetric stretch comes into play. This contribution tends to cancel out the movements of X toward Cd and to reinforce the movement of Y away from Cd. For very large displacements along S_3 the contributions of symmetric and antisymmetric stretch are equal, leaving the Cd-X distance unchanged but increasing the Cd-Y distance at twice the initial rate (Figure 6).

Under the assumption that the smooth curves in Figures 5 and 6 are an approximate representation of the minimum-energy pathway of the decay process, information about the potential energy surface of the reaction can be extracted from them. First, but least interesting, the potential energy should increase in the direction perpendicular to the reaction coordinate. Second, for small displacements from trigonal-bipyramidal geometry the reaction coordinate is assumed to be coincident with a principal axis of the potential energy ellipsoid,[17] Q_4, say, which in the present case is of A''_2 symmetry. It is a linear combination of S_3 and S_4 as can be seen from the relevant part of the potential energy expression

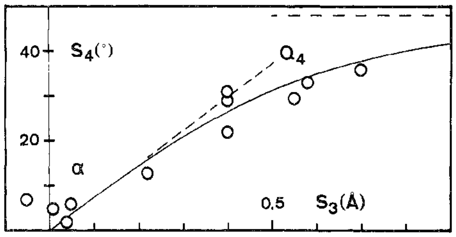

Figure 5. Correlation of the symmetry displacement coordinates S_3 (A''_2) (XCdY antisymmetric stretch) and S_4 (A''_2) (CdS_3 out-of-plane bend).

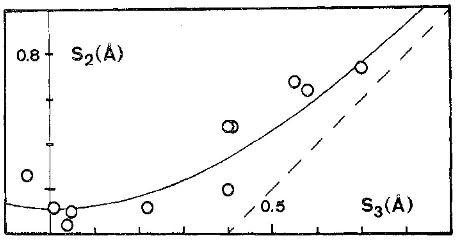

Figure 6. Correlation of the symmetry displacement coordinates S_3 (A''_2) (XCdY antisymmetric stretch) and S_2 (A'_1) (XCdY symmetric stretch).

$$V = {}^1\!/_2 F_{33} S_3{}^2 + {}^1\!/_2 F_{44} S_4{}^2 + F_{34} S_3 S_4 \qquad (18)$$

If α is the angle between Q_4 and S_4, the relationship between α and the potential constants is

$$\tan(2\alpha) = 2F_{34}/(F_{44} - F_{33}) \qquad (19)$$

The numerical value found for α is somewhat larger than that obtained from an infrared spectroscopic force field of the trigonal-bipyramidal molecule PF_5.[16] Third, the sign and relative magnitude of cubic constants may be obtained. As an example, the potential energy in S_2 (A'_1) and S_3 (A''_2) is given through cubic terms including all totally symmetric contributions which may be different from zero by

$$V = {}^1\!/_2 F_{22} S_2{}^2 + {}^1\!/_2 F_{33} S_3{}^2 + F_{233} S_2 S_3{}^2 + F_{222} S_2{}^3 \qquad (20)$$

For small S_3 the derivative along the minimum energy pathway is approximately

$$\frac{dV}{dS_2} = F_{22} S_2 + F_{233} S_3{}^2 + 3F_{222} S_2{}^2 \approx 0 \qquad (21)$$

The relationship connecting S_2 and S_3 along the minimum energy pathway can, in a first approximation, be given as

$$S_3{}^2 \approx a S_2 \qquad (22)$$

Substituting eq 22 into eq 21 and neglecting quadratic terms in S_2 one obtains

$$F_{22}/F_{233} \approx a \qquad (23)$$

The numerical value found for a is −1.3 Å indicating a small value of the cubic constant relative to the quadratic constant. Similar information can be obtained in principle at any point along the minimum-energy pathway for the $XCdS_3Y$ com-

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[15] H. B. Burgi, J. D. Dunitz, and E. Shefter, *J. Amer. Chem. Soc.*, **95**, 5065 (1973).

[16] L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967).

[17] The principal axis rather than the normal coordinate [R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971)] was chosen because of the static nature of the structural information used.

plexes with the Cd displaced from the plane of the three sulfurs.

Discussion

Several objections can be raised against the results presented here: the procedure for bringing the distances Cd· · ·I_{ax}, Cd· · ·S_{ax}, and Cd· · ·O_{ax} to a common basis implicitly assumes that the interactions between Cd and the axial ligands show the same dependence with respect to change of distance, regardless of the nature of the ligands, an assumption that will not hold exactly. As mentioned earlier, the data suggest that the bond increments Δx and Δy do vary from ligand to ligand, but the general shape of the curve is hardly affected and the conclusions for each kind of interaction remain basically unchanged. However, it is clear that the scatter from the regression curves not only is due to experimental errors in the data but also reflects real deviations arising from differences in structure and chemical behavior of the various $XCdS_3Y$ complexes. If the regression (3) describes the behavior of an idealized average $XCdS_3Y$ complex in a homogeneous medium, then the significant deviations from the curve may be interpreted as indications of strain in the various examples observed in different crystal environments. The presence of strain is most clearly shown in the values of S_7 describing the axial bend X-Cd-Y. For the decay of an ideal trigonal bipyramid, the symmetry coordinate S_7 should be zero, whereas the actual values fall into two groups centered around 5 and 14°. The common feature of the second group is a four- or five-membered chelate ring involving an axial and an equatorial substituent. The bond angle S-Cd-X or S-Cd-Y in the ring is about 75°. This must influence the shape of the CdS_3 pyramid and affects principally the coordinates S_7 and S_8. The first group with $S_7 \approx 5°$ does not contain such rings. The variations in the values of the coordinates S_6, S_7, and S_8 also demonstrate the flexibility of the complex $XCdS_3Y$ but do not seem to show any significant correlations with the reaction coordinate.

More serious objections may be raised against the interpretation of crystal data in terms of reaction coordinates. The experimental data obtained for each individual complex represent an equilibrium situation resulting from a complicated interplay of forces. These include effects of crystal packing, constraints due to chelate ring formation, different characteristics of the bonds between Cd and the axial ligands O, S, or I, and changes of these characteristics due to changing environments of the axial ligands—in short, chemical perturbations of many kinds. In spite of the different perturbations, the sequence of *static* pictures (crystal structures) shows a recognizable pattern. Similar but more *dynamical* phenomena, *e.g.,* changes in the solvation of the complexes, influence the processes that occur in chemical reactions. It therefore seems justifiable to use the *average* information obtained in the solid state as model for describing the essential structural features of a reaction coordinate. Hydrogen bonds which have been studied in much more detail by diffraction and spectroscopic methods provide an analogy.[18] Although the potential energy surfaces for specific hydrogen bonds in the solid state are very complicated and only partly unraveled, the composite experimental evidence from many neutron diffraction and infrared spectroscopic studies would seem to give a consistent and continuous picture of a proton-transfer reaction.

The concept of reaction coordinates originates in theory.[19] It can be looked at as an attempt to distinguish the complicated dynamics of a chemical reaction from the underlying driving forces which are commonly represented in terms of potential energy surfaces with their characteristic features such as minima, maxima, saddle points, etc. Defining reaction coordinates depends on an exact knowledge of these features, yet "reactions of interest to most experimental chemists occur between complex molecules in solution and the exact calculation of potential surfaces for such reactions lies far beyond the present state of the art."[20] The ideas presented in this paper may be able to fill a gap until better methods of investigation become available.

It is the purpose of this work to show that information about the nature of a substitution reaction can be obtained from systematic crystal structure studies. Analogous studies of certain other types of reaction are in progress.[15] Although many of the results are qualitative, it should be possible to improve the quantitative aspects by more extensive studies based on a wider and more judicious choice of compounds. Careful analysis of large sets of data could then provide guidelines for spectroscopic, thermodynamic, and mechanistic investigations.

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(18) For a review see W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., and Amsterdam, 1968. P. Merlet, S. D. Peyerimhoff, and R. J. Buenker, *J. Amer. Chem. Soc.*, 94, 8301 (1972).

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