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A Study of the Crystal and Molecular Structure of $BeCl_2(NCCH_3)_2$ by X-Ray Diffraction and MO Calculations

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A comparative study of the molecular structure of the 1:2 complex of beryllium chloride with methyl cyanide is carried out by X-ray diffraction and MO calculations of both CNDO and ab initio type. The site symmetry of the beryllium atom in $BeCl_2(NCCH_3)_2$ is shown to be 4-coordinate, deformed tetrahedral; a novel feature lies in a slight "crab-claw" configuration assumed by the nitrile ligands, which are coordinated by nitrogen to the metal atom. Experimentally determined interatomic distances and bond angles are compared with those predicted by MO treatment involving energy minimization. Application of the computational method in the case of the microcrystalline, nonisotypical compound $BeCl_2(NCCl)_2$ suggests that the latter molecule also has a distorted tetrahedral structure, but with Cl–Be–Cl and N–Be–N bond angles which are respectively greater and smaller than those of the corresponding methyl cyanide complex.

Introduction

Although addition compounds of beryllium chloride with various aliphatic and aromatic nitriles have been known for many years[1], very little work appears to have been reported on the structural features of these complexes. In connection with the recent preparation of the new compound $BeCl_2(NCCl)_2$,[2] it appeared of interest to examine the 1:2 type of adduct from the standpoint of a simple molecular model based on 4-coordinate beryllium. It is expedient, for this purpose, to consider the cyanogen chloride complex together with the analogous methyl cyanide derivative since it would be expected that the low structural complexity of these nitriles should render them readily accessible both to crystallographic and computational treatment. In the present work, the data obtained from an X-ray study of the molecular structure of $BeCl_2(NCCH_3)_2$ are used to verify MO calculations which are subsequently applied to the microcrystalline compound $BeCl_2(NCCl)_2$. It is useful, to this end, to compare the predictions furnished by the semi-empirical and *ab initio* methods both with each other and with the established crystallographic data.

Experimental

Synthesis

The nitrile adducts of anhydrous beryllium chloride were prepared by procedures described elsewhere[1,2], using cyanogen chloride and methyl cyanide which had been previously purified and dried by distillation over phosphorus pentoxide and calcium hydride, respectively. Single crystals of $BeCl_2(NCCH_3)_2$ suitable for X-ray structural studies were obtained by slow cooling of heated solutions of the adduct in excess methyl cyanide under nitrogen, followed by evaporation of the solvent *in vacuo*. All operations involving handling and transfer of the compounds were carried out under dry nitrogen.

Crystal Studies

Lattice constants were measured from precession photographs. Crystal data are shown in Table I. Line distances were measured on films to the nearest 1/100 millimeter and a correction for film shrinkage was applied. The density was measured by pycnometry in carefully dried petroleum ether[2].

A single crystal with dimensions 0.43 × 0.33 × 0.33 mm used for data collection was placed in a glass capillary in a glove box. After sealing, this tube was set on a

TABLE I. Crystal Data.

a = 12.31 ± 0.01 Å	Systematic Absences
b = 9.984 ± 0.008 Å	
c = 6.390 ± 0.006 Å	(0kl) : k + l = 2n + 1
V = 785 ± 2 Å^3	(h0l) : h = 2n + 1
d_{exp} = 1.41 ± 0.05	
d_{RX} = 1.38 ± 0.05	Space Groups : $Pna2_1$ or
Z = 4	Pnma

30 cm diameter eulerian cradle. MoKα radiation (λ = 0.71069) was supplied by a stabilized CGR Θ 60 generator. Diffracted intensities were measured with a scintillation counter equipped with a pulse height analyser adjusted to MoKα energy in such a way that 90% of the diffracted intensity was counted. An oriented graphite monochromator was placed in front of the counter window.

731 independent reflections for which the Bragg angle was less than 25°, were recorded at room temperature, with ω–2Θ scan, after manual setting of the crystal. A scan of 100 seconds corresponds to 1.25° in the Bragg angle. Background was measured for 30 seconds at both ends of scan in fixed position.

Three reflections 060, 600 and 111 were chosen as standards and their intensities measured twice a day. No anomaly was observed. Forty reflections for which counting rates were greater than 10,000 c/s, were corrected for counting losses[3]. The intensities were corrected for Lorentz, absorption and (in the least-squares refinement) secondary extinction effects. The absorption coefficient μ was determined to be 7.56 cm^{-1}. The resulting transmission factors were in the range 0.73 to 0.81. For every structure factor F, a standard deviation σ is computed:

$$\sigma = \frac{F \times \Delta C}{2C}$$

where C is the integrated intensity and ΔC the error in integrated intensity.

If the observed structure factor was less than or equal to its standard deviation σ, it was considered as a zero reflection and the structure factor was set at one half the value of the standard deviation. During least squares refinements, the reciprocal of the standard deviation was used as a weighting factor.

Results and Discussion

Structural Determination of $BeCl_2(NCCH_3)_2$

The test of Howels, Phillips and Rogers[4] (Figure 1) and the computation of second and third order moments on diffracted intensities[5] (Table II), suggested a centered space group. Accordingly, Pnma was chosen. From a three-dimensional Patterson map, the chlorine atoms were found in the y = 1/4 symmetry plane. A least-squares refinement[6] of these positions, followed by Fourier difference synthesis, revealed the positions of the carbon, nitrogen and beryllium atoms. Atomic positions of all atoms were refined by least squares using the form factors of Cromer and Waber[7] and isotropic temperature factors. The resulting value of R was 0.14, where $R = \Sigma|(F_{calc}-F_{obs})|/\Sigma F_{obs}$. When anisotropic temperature factors were introduced and the form factors corrected for the real part of the anomalous dispersion, R was reduced to 0.06. After elimination of 15 reflections for which too large differences

TABLE II. Moments on Diffracted Intensities.

	Experimental Values	Theoretical Values Centric Case	Acentric Case
Second Order Moment	3.425	3.064	2.086
Third Order Moment	19.975	16.107	7.054

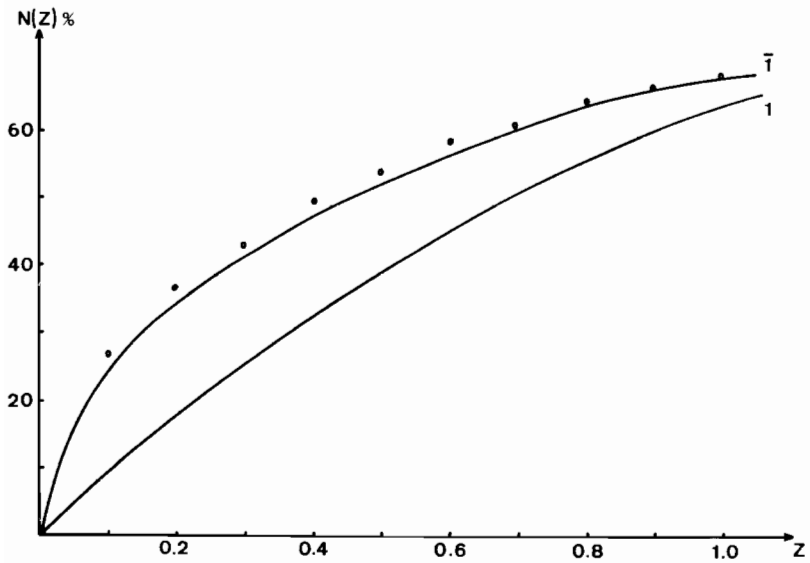

Figure 1. Rogers' test: points are experimental values. (1) is related to acentric case and ($\bar{1}$) to centric case.

(F_{obs}–F_{calc}) showed an error of manual adjustment, the R factor decreased to 0.051. A final refinement, including an isotropic extinction coefficient[8], converged to:

Non weighted R, including 201 zeros	0.066
Non weighted R, excluding 201 zeros	0.051
Weighted R, including 201 zeros	0.048
Weighted R, excluding 201 zeros	0.046

where weighted R is: $R_w = (\Sigma(w|F_{calc}-F_{obs}|)^2/\Sigma(wF_{obs})^2)^{1/2}$. The value of the secondary extinction parameter is $g = 0.34 \times 10^{-5}$.

Throughout the refinement of the structure, the minimized function was weighted R.

A Fourier difference synthesis did not show peaks higher than the error on electron density (0.44 e/Å^3); thus hydrogen atoms could not be located.

The final positional parameters and the thermal parameters are given in Table III. Observed and calculated structural factors are presented in Table IV. The value of F(000) is 1,845. Interatomic distances and bond angles are given in Table V.

Description and Discussion of the Structure

The beryllium atom is tetrahedrally surrounded by two chlorine atoms and two nitrogen atoms of the methyl cyanide molecules (Figure 2). The chlorine

TABLE III. Atomic Parameters and Anisotropic Thermal Vibration Components, $\exp[-2\pi^2(U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Standard deviations are in parenthesis.

Atoms	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	0.07362(9)	1/4	–0.2405(2)	0.0522(6)	0.0609(5)	0.0385(6)	0.0	0.0047(4)	0.0
Cl(2)	–0.14552(8)	1/4	0.0755(2)	0.0374(5)	0.0569(5)	0.0511(6)	0.0	–0.0014(4)	0.0
Be	0.0138(4)	1/4	0.0480(7)	0.037(2)	0.037(3)	0.033(2)	0.0	–0.006(2)	0.0
N	0.0684(2)	0.3833(3)	0.1858(4)	0.0453(8)	0.046(2)	0.045(1)	–0.005(1)	–0.002(1)	–0.003(1)
C(1)	0.1101(2)	0.4586(3)	0.2898(5)	0.041(2)	0.039(1)	0.043(2)	–0.000(2)	0.001(1)	0.001(2)
C(2)	0.1642(3)	0.5531(4)	0.4246(6)	0.061(2)	0.049(1)	0.058(2)	–0.007(1)	–0.010(2)	–0.017(2)

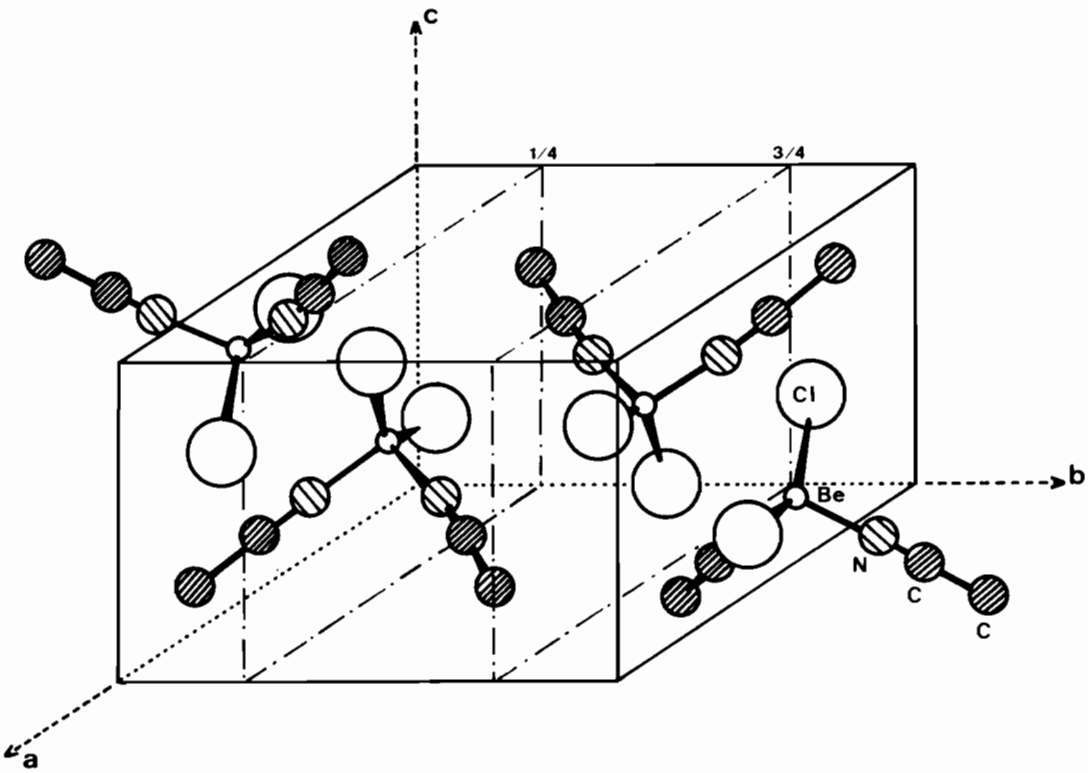

Figure 2. Occupancy of the unit cell.

TABLE IV. Observed and Calculated Structural Factors: columns are k, l, F observed, F calculated.

H = 0			
2	0	302	329
4	0	421	431
6	0	409	404
8	0	218	205
10	0	173	170
3	1	340	340
5	1	95	100
7	1	34	29
9	1	10	15
11	1	60	58
0	2	272	296
2	2	39	11
4	2	35	18
6	2	49	39
8	2	49	53
10	2	10	3
1	3	345	355
3	3	521	525
5	3	192	190
7	3	246	248
9	3	99	100
2	4	100	98
4	4	121	122
6	4	56	54
8	4	52	49
10	4	29	36
1	5	43	45
5	5	10	13
7	5	11	12
0	6	169	165
2	6	139	138
4	6	169	166
6	6	104	104
1	7	88	88
3	7	16	29
H = 1			
0	1	195	228
1	1	131	153
2	1	344	330
3	1	327	293
4	1	96	87
5	1	66	73
6	1	121	117
7	1	95	92
8	1	121	124
9	1	42	45
10	1	21	22
11	1	25	24
0	2	330	305
1	2	250	241
2	2	64	62
3	2	8	7
4	2	206	211
5	2	51	46
6	2	111	107
7	2	108	109
8	2	13	7
9	2	34	33
10	2	66	67
11	2	11	13
0	3	83	73
1	3	76	67
2	3	24	21
3	3	23	30
4	3	123	117
5	3	35	32
6	3	3	11
7	3	69	70
8	3	36	40
9	3	19	2
10	3	25	28
0	4	152	155
1	4	113	113
2	4	79	76
3	4	140	141
4	4	30	35
6	4	75	72
7	4	10	3
8	4	42	40
9	4	52	56
10	4	11	22
0	5	10	19
1	5	76	78
2	5	10	5
3	5	101	99
4	5	68	73
5	5	10	0
6	5	10	9
7	5	77	78
8	5	11	17
0	6	48	52
1	6	40	45
2	6	10	2
3	6	10	0
4	6	45	52
5	6	28	25
6	6	11	13
7	6	33	30
0	7	42	40
1	7	19	22
2	7	88	84
3	7	23	26
4	7	22	31
H = 2			
0	0	262	302
1	0	51	89
2	0	239	196
3	0	146	169
4	0	24	1
5	0	74	73
6	0	97	90
7	0	10	12
8	0	106	106
9	0	14	27
10	0	22	10
11	0	48	48
0	1	92	72
1	1	88	88
3	1	341	317
4	1	322	308
5	1	119	117
6	1	143	141
7	1	50	50
8	1	110	113
9	1	24	30
10	1	35	39
11	1	41	40
0	2	341	328
1	2	458	459
2	2	79	90
3	2	77	95
4	2	87	71
5	2	297	293
6	2	92	90
8	2	52	56
9	2	124	124
10	2	18	28
11	2	26	32
0	3	54	53
1	3	96	93
2	3	7	18
3	3	82	87
4	3	14	7
5	3	101	99
6	3	10	3
7	3	21	26
8	3	30	35
9	3	23	26
10	3	11	2
0	4	145	141
1	4	190	191
3	4	110	111
4	4	92	96
5	4	153	156
6	4	74	73
7	4	54	57
8	4	36	37
0	5	144	138
1	5	75	73
2	5	185	187
3	5	53	54
4	5	96	93
5	5	19	25
6	5	97	96
7	5	48	48
8	5	84	87
0	6	16	3
1	6	21	25
2	6	48	49
3	6	35	36
4	6	40	45
5	6	23	8
6	6	11	14
7	6	11	7
0	7	87	83
1	7	64	67
2	7	47	50
3	7	33	35
4	7	32	35
H = 3			
1	1	7	20
2	1	337	312
3	1	108	102
4	1	120	117
5	1	85	81
6	1	59	59
7	1	9	13
8	1	85	86
9	1	10	19
10	1	10	5
11	1	10	15
1	2	183	172
2	2	71	58
3	2	94	103
4	2	183	181
5	2	148	149
6	2	29	33
7	2	36	37
8	2	3	12
9	2	35	32
10	2	43	41
11	2	35	39
0	3	72	65
1	3	105	107
2	3	8	14
3	3	9	7
4	3	17	18
5	3	51	54
6	3	10	13
7	3	83	93
9	3	19	6
10	3	11	2
1	4	134	140
2	4	47	43
3	4	10	0
4	4	85	84
5	4	117	118
6	4	9	23
7	4	16	15
8	4	44	44
9	4	35	41
0	5	83	82
1	5	90	90
2	5	64	67
3	5	45	45
4	5	51	53
5	5	10	6
6	5	28	33
7	5	82	80
8	5	48	45
0	6	45	44
1	6	10	5
2	6	10	5
3	6	18	17
4	6	63	64
5	6	9	1
6	6	11	17
0	7	11	1
1	7	11	9
2	7	59	58
3	7	13	15
H = 4			
0	0	506	512
1	0	537	542
2	0	79	65
3	0	60	82
5	0	293	289
6	0	153	148
7	0	173	174
8	0	51	44
9	0	133	131
10	0	87	85
11	0	29	36
0	1	7	4
1	1	69	66
2	1	201	195
3	1	64	54
4	1	239	239
5	1	71	60
6	1	77	75
7	1	29	29
8	1	10	1
9	1	32	35
10	1	43	47
11	1	11	10
0	2	48	58
1	2	220	211
2	2	82	77
3	2	50	52
4	2	7	2
5	2	35	41
6	2	15	17
7	2	96	95
8	2	10	6
9	2	43	43
10	2	10	9
0	3	122	128
1	3	137	140
2	3	322	325
3	3	223	227
4	3	211	211
5	3	46	45
6	3	124	126
7	3	117	119
8	3	111	111
10	3	40	40
0	4	21	17
1	4	105	110
2	4	28	33
3	4	113	111
4	4	10	11
5	4	74	75
6	4	10	13
7	4	45	48
8	4	11	9
0	5	104	104
1	5	10	5
2	5	39	42
3	5	10	16
4	5	37	34
5	5	7	6
6	5	41	42
7	5	11	2
8	5	13	27
0	6	88	83
1	6	98	95
2	6	60	58
3	6	100	100
4	6	62	64
5	6	106	104
6	6	47	50
0	7	88	84
1	7	12	1
2	7	37	44
3	7	20	9
H = 5			
0	1	69	62
1	1	242	241
2	1	12	7
3	1	232	222
4	1	8	23
5	1	86	80
6	1	144	143
7	1	10	2
9	1	66	66
10	1	19	2
11	1	20	21
0	2	331	336
1	2	15	2
2	2	84	73
3	2	7	3
4	2	73	74
5	2	86	85
6	2	116	120
7	2	41	45
8	2	56	55
9	2	8	14
10	2	49	43
0	3	41	37
1	3	49	48
2	3	80	77
3	3	93	90
4	3	44	38
5	3	10	15
6	3	35	33
7	3	10	
8	3	32	
9	3	15	
10	3	22	
0	4	107	1
1	4	10	
2	4	127	1
3	4	19	
4	4	161	1
5	4	47	
6	4	88	
7	4	26	
8	4	15	
9	4	11	
0	5	23	
1	5	10	
2	5	55	
3	5	95	
4	5	28	
5	5	15	
6	5	10	
7	5	18	
0	6	41	
1	6	34	
2	6	10	
3	6	11	
4	6	11	
5	6	55	
6	6	11	
0	7	11	
1	7	59	
2	7	33	
H = 6			
0	0	101	
1	0	298	
2	0	22	
4	0	87	
5	0	80	
6	0	10	
7	0	179	
8	0	65	
9	0	47	
10	0	24	
0	1	11	
1	1	150	
2	1	70	
3	1	352	
4	1	82	
5	1	138	
6	1	10	
7	1	110	
8	1	32	
9	1	51	
10	1	21	
0	2	413	
1	2	19	
2	2	164	
3	2	9	

and beryllium atoms are in the symmetry planes y = 1/4 and y = 3/4. The bond angles (Cl–Be–Cl = 116.8(2)°; N–Be–N = 100.5(2)°) are typical for tetrahedral distortion. In fact, such distortion is also observed in other beryllium compounds such as $Be(CH_3)_2(NC_7H_{13})_2$[9] and $(BeCH_3(C{\equiv}C{-}CH_3)N(CH_3)_3)_2$[10]. It seems that the chlorine and nitrogen atoms undergo site shifting in order to maintain normal Van der Waals contacts. Indeed, the Cl–N and Cl–Cl distances (3.031(3) Å and 3.369(2) Å, respectively) are similar to those found in $NbCl_5(NCH)$[11], $TiCl_4(NCH)_2$[12], $VCl_4(NCH)_2$[13] and $NbOCl_3(NCCH_3)_2$[14] (Table VI).

The beryllium–chlorine distances (1.970(4) Å and 1.985(4) Å) are longer than those found in monomeric $BeCl_2$ (1.75 ± 0.02 Å) by electron diffraction[15]. A similar elongation of the Be–Cl bond is also found

TABLE IV. (Cont.)

4	2	177	175
5	2	84	84
6	2	164	158
7	2	30	37
8	2	96	96
9	2	25	23
10	2	74	74
0	3	195	191
1	3	14	6
2	3	120	124
3	3	10	2
4	3	165	166
5	3	32	37
6	3	89	89
7	3	10	16
8	3	52	52
9	3	11	10
0	4	158	156
1	4	24	17
3	4	21	34
4	4	107	106
5	4	10	0
6	4	81	81
7	4	23	22
8	4	37	35
0	5	10	7
1	5	139	142
2	5	25	33
3	5	129	129
4	5	24	19
5	5	70	70
6	5	11	6
7	5	95	98
0	6	19	25
1	6	57	58
2	6	22	31
3	6	68	69
4	6	21	28
5	6	49	50

H = 7

0	1	74	84
1	1	8	22
2	1	204	205
3	1	57	61
4	1	164	163
5	1	47	50
6	1	84	82
7	1	24	28
8	1	71	71
9	1	17	10
10	1	37	38
0	2	2	1
1	2	120	122
2	2	5	0
3	2	172	169
4	2	10	1
5	2	144	149
6	2	10	7
7	2	44	43
8	2	10	11
9	2	39	40
0	3	125	127
1	3	11	1
2	3	44	47
3	3	50	51
4	3	16	15
5	3	13	14
6	3	38	46
7	3	12	23
9	3	11	1
0	4	91	90
1	4	137	140
2	4	51	53
3	4	10	16
4	4	27	27
5	4	61	66
6	4	16	12
7	4	68	64
8	4	17	15
0	5	111	114
1	5	10	7
2	5	75	73
3	5	10	12
4	5	28	36
5	5	12	12
6	5	47	49
0	6	44	46
1	6	36	35
2	6	11	6
3	6	56	55
4	6	21	18

H = 8

0	0	74	81
1	0	258	254
2	0	34	32
3	0	74	74
4	0	68	75
5	0	200	196
6	0	21	25
7	0	58	55
8	0	31	38
9	0	85	79
0	1	39	34
1	1	124	124
2	1	42	39
3	1	153	156
4	1	10	14
5	1	181	182
6	1	10	17
7	1	10	8
8	1	10	3
9	1	56	57
0	2	174	171
1	2	14	23
2	2	197	197
3	2	10	2
4	2	67	67
5	2	10	6
6	2	108	110
7	2	10	3
8	2	98	98
9	2	11	15
0	3	71	72
1	3	12	4
2	3	186	191
3	3	19	24
4	3	100	102
5	3	18	27
6	3	76	73
7	3	10	11
8	3	81	79
0	4	56	58
1	4	10	11
2	4	100	103
3	4	10	10
4	4	61	60
5	4	18	16
6	4	44	45
7	4	11	6
0	5	20	20
1	5	110	110
2	5	10	3
3	5	68	70
4	5	11	0
5	5	74	75
6	5	11	5
0	6	9	5
1	6	63	67
2	6	11	13
3	6	49	51

H = 9

0	1	22	21
1	1	112	114
2	1	48	45
3	1	83	84
4	1	10	2
5	1	54	57
6	1	10	10
7	1	59	55
8	1	30	30
9	1	25	36
0	2	107	107
1	2	71	67
2	2	60	65
3	2	47	50
4	2	27	26
5	2	50	51
6	2	49	50
7	2	11	1
8	2	36	40
0	3	84	86
1	3	33	38
2	3	30	30
3	3	10	17
4	3	3	4
5	3	10	1
6	3	10	11
7	3	24	21
8	3	18	11
0	4	62	60
1	4	11	1
2	4	74	75
3	4	39	43
4	4	85	88
5	4	19	19
6	4	48	49
0	5	56	54
1	5	10	11
2	5	54	50
4	5	11	16
5	5	34	29

H = 10

0	0	128	121
1	0	139	138
2	0	105	120
3	0	104	106
4	0	54	52
5	0	9	10
6	0	87	84
7	0	115	115
8	0	52	52
0	1	57	51
1	1	37	39
2	1	72	74
3	1	49	52
4	1	119	121
5	1	11	15
6	1	31	39
7	1	58	57
8	1	11	12
0	2	77	76
1	2	101	105
2	2	10	0
3	2	59	56
4	2	63	63
5	2	40	38
6	2	12	23
7	2	66	65
8	2	11	4
0	3	122	121
1	3	81	78
2	3	56	55
3	3	80	80
4	3	98	98
5	3	67	67
6	3	56	58
7	3	26	29
0	4	22	33
1	4	53	53
2	4	10	4
3	4	47	49
4	4	11	20
5	4	39	37
6	4	11	15
0	5	53	58
1	5	11	15
2	5	47	47
3	5	35	35

H = 11

0	1	67	71
1	1	34	39
2	1	45	46
3	1	102	100
4	1	53	53
5	1	26	26
6	1	37	36
7	1	41	41
0	2	25	29
1	2	56	57
2	2	62	61
3	2	55	58
4	2	70	68
5	2	43	41
6	2	34	38
7	2	33	33
0	3	13	8
1	3	53	52
2	3	10	21
3	3	10	18
4	3	10	8
5	3	11	17
6	3	11	4
0	4	111	109
1	4	29	29
3	4	28	35
4	4	13	17
0	5	39	37

H = 12

0	0	83	85
1	0	45	45
3	0	52	54
4	0	29	29
5	0	87	86
6	0	43	42
0	1	87	87
1	1	42	43
2	1	61	60
3	1	35	32
4	1	114	114
5	1	59	61
6	1	41	44
0	2	26	26
1	2	112	108
2	2	62	60
3	2	89	84
4	2	11	14
5	2	44	46
6	2	11	23
0	3	29	27
1	3	40	37
2	3	55	55
3	3	46	50
4	3	11	17
0	4	11	19
1	4	43	40
2	4	39	39

H = 13

0	1	67	66
1	1	52	52
2	1	63	59
3	1	47	48
4	1	35	42
5	1	43	49
0	2	10	8
1	2	59	58
2	2	53	53
3	2	11	8
4	2	30	37
0	3	26	40
1	3	30	42
2	3	11	17

H = 14

0	0	109	106
1	0	11	6
2	0	131	129
3	0	33	26
0	1	22	19
1	1	3	2
2	1	11	9
3	1	11	14
0	2	11	0
1	2	11	3

in the compound $BeClC_5H_5$ (1.839(7) Å)[16]. Conversely, the observed N–C triple bond length of 1.131 (3) Å in the nitrile complex is 0.03 Å shorter than in free methyl cyanide[17]. As will be seen from the following theoretical consideration of these compounds, such variations can be interpreted in terms of MO calculations of electron distribution in the consituent molecules prior to and following coordination.

Molecular Orbital Calculations

Computational Methods

SCF calculations for the methyl cyanide and cyanogen chloride complexes were carried out by both *ab initio* and CNDO/2 methods. For the latter approximation, the valence atomic orbitals were represented by a Slaterian basis set of simple zeta type. In the *ab initio* treatment, the beryllium atom was described by

TABLE V. Interatomic Distances (Å) and Bond Angles (°) with Standard Deviations σ.

Distances		σ	Angles		σ
Be–Cl(1)	1.985	0.004	Cl(1)–Be–Cl(2)	116.8	0.2
Be–Cl(2)	1.970	0.004	N–Be–N	100.5	0.2
Be–N	1.729	0.003	N–Be–Cl(1)	109.9	0.2
N–C(1)	1.131	0.003	Be–N–C(1)	171.7	0.2
C(1)–C(2)	1.439	0.003	N–C(1)–C(2)	178.7	0.2
Cl(1)–Cl(2)	3.369	0.002			
Cl(1)–N	3.031	0.003			
Cl(2)–N	3.032	0.003			
N–N	2.658	0.003			

TABLE VI. Comparison of Cl–Cl and Cl–N Distances Found in Various Coordination Compounds.

Compounds	Cl–Cl (Å)	Cl–N (Å)
$TiCl_4(NCH)_2$	3.34	3.04
$NbCl_5(NCH)$	3.33	3.05
$VCl_4(NCH)_2$	3.30	2.98
$NbOCl_3(NCCH_3)_2$	3.45	3.08
this work	3.37	3.03

a 7s Gaussian basis set contracted in (4s)[18] and modified by addition of a 2p function with the orbital exponent 0.7. A (7s, 3p) basis contracted in (2s, 1p) was used for the carbon and nitrogen atoms, with a (10s, 6p) basis contracted in (3s, 2p) and a (3s) basis contracted in (1s)[19] for the chlorine and hydrogen atoms respectively.

Theoretical Consideration of the Ligand Molecules

Ab initio optimization of the Be–Cl bond length in monomeric beryllium chloride led to a value of 1.79 Å, in satisfactory agreement with the experimentally determined value[15]. The corresponding total energy calculated for $BeCl_2$ is –931.819 a.u. for the following ground state:
$1\sigma_g^+(-104.192)$, $1\sigma_\mu^+(-104.192)$, $2\sigma_g^+(-10.094)$, $2\sigma_\mu^+(-10.091)$, $3\sigma_g^+(-7.793)$, $3\sigma_\mu^+(-7.792)$, $1\pi_\mu(-7.789)$, $1\pi_g(-7.788)$, $4\sigma_g^+(-4.820)$, $5\sigma_g^+(-1.031)$, $4\sigma_\mu^+(-1.025)$, $6\sigma_g^+(-0.530)$, $5\sigma_\mu^+(-0.503)$, $2\pi_\mu(-0.466)$, $2\pi_g(-0.448)$.

In the $5\sigma_g^+$ molecular orbital, the Be–Cl bond (overlap population 0.49 e) is mainly described by interaction of the beryllium 2s orbitals with the chlorine 3s orbitals. For the $6\sigma_g^+$ molecular orbital, the metal-halogen bond involves overlap of 2s and $3p_z$ orbitals in these respective atoms. Overlap of the $2p_x$ and $2p_y$ orbitals of beryllium with the corresponding chlorine orbitals in the $2\pi_\mu$ molecular orbital results in a weak π contribution in the halogen. The last occupied molecular orbital ($2\pi_g$) is essentially composed of 3p atomic orbitals localized on the chlorine atoms.

The Mulliken population analysis (Table VII) indicates that the beryllium atom has a relatively high positive charge (1.12 e). This charge arises from the transfer of 1.40 e from the beryllium 2s orbital to the chlorine atoms, accompanied by a back-donation of 0.24 e from these atoms to the unoccupied $2p_\sigma$ orbital of beryllium. On the other hand, the contribution represented by transfer towards the beryllium $2p_\pi$ orbitals is very small (0.06 e).

The CNDO/2 description of the various valence orbitals gives rise to the following ground state:
$1\sigma_\mu^+(-1.180)$, $1\sigma_g^+(-1.142)$, $2\sigma_\mu^+(-0.679)$, $2\sigma_g^+(-0.649)$ $1\pi_\mu(-0.640)$, $1\pi_g(-0.552)$.

As in the case of the non-empirical calculation, the two occupied molecular orbitals $1\pi_\mu$ and $1\pi_g$ are respectively associated with a Be–Cl π bond and atomic orbitals localized on the chlorine atoms. The σ-type molecular orbitals differ from those obtained by *ab initio* in that they involve a greater degree of participation of the 2p atomic orbitals of beryllium. It is noteworthy that the electron transfer from the beryllium 2s orbital to the chlorine atoms is virtually identical to that required by *ab initio* (1.40 e). Conversely, the back-donation from chlorine to the beryllium 2p orbitals involves both σ and π contributions, with the result that the residual charges on the remaining atoms of the molecule are very weak. Accordingly, it would appear that the CNDO/2 treatment overestimates the bonding contribution of the vacant 2p orbitals of the beryllium.

The *ab intio* calculation of the electronic structure of the methyl cyanide molecule is not anomalous, and differs from the CNDO/2 calculation only in that the latter method predicts a weak charge on the methyl carbon atom (Table VIII). This shortcoming arises from the inadequate description of the hydrogen atoms by CNDO.

Theoretical Study of the Complexes

The geometry considered in the various LCAO–MO calculations corresponds to the structure determined

TABLE VII. Calculated Electronic Structure of $BeCl_2$.

		Ab Initio	CNDO/2
	2s	0.611	0.676
Be	$2p_\sigma$	0.238	0.768
	$2p_\pi$	0.062	0.540
	q	1.12	0.102
	3s	1.941	1.863
	$3p_\sigma$	1.666	1.208
Cl	$3p_\pi$	4.00	3.688
	$3d_\sigma$	–	0.206
	$3d_\pi$	–	0.040
	q	–0.56	–0.01

TABLE VIII. Calculated Electronic Structure of CH_3CN and ClCN.

		CH_3CN *ab initio*	CH_3CN CNDO/2	ClCN CNDO/2
N	2s	1.695	1.647	1.649
	$2p_\sigma$	1.460	1.343	1.346
	$2p_\pi$	2.030	2.170	2.080
	q	–0.18	–0.16	–0.07
C_1	2s	0.919	1.084	1.090
	$2p_\sigma$	0.995	0.947	0.952
	$2p_\pi$	1.995	1.880	1.884
	q	0.10	0.09	0.07
C_2	2s	1.235	1.003	–
	$2p_\sigma$	1.003	1.037	–
	$2p_\pi$	2.431	1.978	–
	q	–0.66	–0.02	–
Cl	3s	–	–	1.892
	$3p_\sigma$	–	–	0.844
	$3p_\pi$	–	–	3.916
	$3d_\sigma$	–	–	0.226
	$3d_\pi$	–	–	0.116
	q	–	–	0.01
H	1s	0.754	0.969	–
	q	0.25	0.03	–

by X-ray analysis for $BeCl_2(NCCH_3)_2$ and is represented by the point group C_{2v} (Figure 3). In view of the number of atoms contained in the methyl cyanide complex, no geometrical optimization was carried out for this molecule by *ab initio*. However, the CNDO/2 method was applied to both the methyl cyanide and the cyanogen chloride adducts in the optimization of distances and angles for the four bonds connected with the beryllium atom (Table IX).

It is evident from the CNDO energy minimization calculations for the two complexes that the respective Be–Cl and Be–N bond lengths remain virtually unchanged when the nitrile chlorine atoms are formally replaced by methyl groups. On the other hand, it is

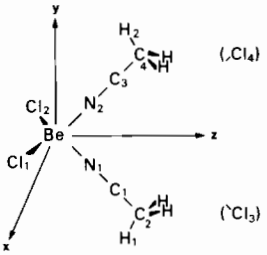

Figure 3. Configuration and system of axes for $BeCl_2(NCR)_2$ (R = CH_3, Cl).

found that the N–Be–N bond angle in $BeCl_2(NCCl)_2$ is of the order of $9° \pm 1$ smaller than that of a $BeCl_2(NCCH_3)_2$ molecule with corresponding geometry (respectively equivalent interatomic distances and linear Be–N–C–R bonds). The difference thus observed in the angle formed by the nitrile ligands with the metal atom is not appreciably changed when allowance is made for the experimentally determined non-linearity of the Be–N–C–C bond system (Table IX).

A general description of the ground state of $BeCl_2(NCCH_3)_2$ as calculated by *ab initio* is presented in Table X.

The last occupied MO's ($17a_1$, $11b_2$, $4a_2$ and $9b_1$) are composed entirely of 3p atomic orbitals localized on the chlorine atoms; the $15a_1$, $7b_1$, $3a_2$ and $10b_2$ MO's represent the CH_3CN ligands. The interactions described by the $11a_1$ (2s (Be), 3s Cl)) and $16a_1$ (2s (Be), 3s (Cl), $3p_x$ (Cl)) MO's account mainly for the Be–Cl bonds, and the MO's denoted by $11a_1$ (2s (Be), 2s (N), $2p_z$ (N)), $13a_1$ ($2p_z$ (Be), 2s (N), $2p_z$ (N), $2p_z$ (Cl)) and $8b_2$ ($2p_y$ (Be), 2s (N), $2p_y$ (N), $2p_y$ (Cl)) are characteristic for the Be–N bonds.

The CNDO/2 calculation for the methyl cyanide complex leads to the following representation of the ground state:

$1a_1(-1.688)$, $1b_2(-1.668)$, $2a_1(-1.489)$, $2b_2(-1.445)$, $3a_1(-1.110)$, $1b_1(-1.072)$, $4a_1(-0.976)$, $3b_2(-0.970)$, $1a_2(-0.929)$, $4b_2(-0.916)$, $2b_1(-0.903)$, $5a_1(-0.893)$, $6a_1(-0.786)$, $5b_2(-0.781)$, $3b_1(-0.712)$, $7a_1(-0.699)$, $2a_2(-0.668)$, $6b_2(-0.683)$, $8a_1(-0.503)$, $4b_1(-0.478)$, $7b_2(-0.430)$, $3a_2(-0.426)$, $5b_1(-0.401)$, $9a_1(-0.397)$.

TABLE IX. CNDO/2 Optimization of Be–Cl and Be–N Bonds in the Molecules $BeCl_2(NCR)_2$.

Compound		d_{Be-Cl} (Å)	d_{Be-N}(Å)	Cl–Be–Cl	N–Be–N
$BeCl_2(NCCl)_2$		1.85	1.51	126°	120°
$BeCl_2(NCCH_3)_2$	a	1.85	1.52	123°	128.5°
	b	1.85	1.51	123°	130°
	c	1.985	1.729	116.8°	100.5°
		1.970			

[a] Calculations based on the geometry computed for $BeCl_2(NCCl)_2$ (linear Be–N–C–R bonds). [b] Calculations based on the results of X-ray structural analysis (non-linear Be–N–C–R bonds). [c] Values found by X-ray structural determination.

TABLE X. *Ab initio* Calculation of the Ground State of $BeCl_2(NCCH_3)_2$.

Symmetry	Energy (a.u.)	Overlap population					Type of Atomic Orbital
		Be–N_1	Be–Cl	N_1–C_1	C_1–C_2	C_2–H	
$9b_1$	−0.303	–	–	–	–	–	$3p_x(Cl)$, $3p_z(Cl)$
$4a_2$	−0.318	–	–	–	–	–	$3p_y(Cl)$
$11b_2$	−0.326	–	–	–	–	–	$3p_z(Cl)$
$17a_1$	−0.328	0.009	0.013	−0.003	–	–	$3p_z(Cl)$, $3p_x(Cl)$
$8b_1$	−0.351	–	0.055	–	−0.002	–	$2p_x(Be)$, $3p_x(Cl)$, $3p_z(Cl)$
$16a_1$	−0.394	−0.037	0.155	−0.005	–	–	2s(Be), $3p_x(Cl)$, 3s(Cl)
$10b_2$	−0.610	–	–	0.228	−0.106	0.089	$2p_y(N)$, $2p_y(C_1)$
$3a_2$	−0.618	–	–	0.217	−0.105	–	$2p_x(N)$, $2p_x(C_1)$
$7b_1$	−0.625	0.002	–	0.203	−0.103	–	$2p_x(N)$, $2p_x(C_1)$, $2p_x(C_2)$
$15a_1$	−0.630	0.002	–	0.188	−0.103	0.109	$2p_z(N)$, $2p_z(C_1)$, $2p_z(C_2)$, 1s(H)
$9b_2$	−0.735	0.009	–	0.003	0.077	0.179	1s(H), $2p_y(C_2)$
$2a_2$	−0.732	–	–	0.057	0.098	–	$2p_x(N)$, $2p_x(C_1)$, $2p_x(C_2)$
$14a_1$	−0.739	0.003	–	0.048	0.097	0.123	$2p_y(C_1)$, $2p_z(C_2)$, 1s(H)
$6b_1$	−0.739	0.002	–	0.061	0.098	–	$2p_y(N)$, $2p_z(C_1)$, $2p_z(C_2)$
$8b_2$	−0.741	0.024	–	−0.078	0.057	–	$2p_y(Be)$, 2s(N), $2p_y(N)$, $2p_y(C_1)$
$13a_1$	−0.773	0.028	–	−0.061	0.076	0.075	$2p_z(Be)$, 2s(N), $2p_z(N)$, $2p_z(C_1)$, $2p_z(C_2)$
$7b_2$	−0.816	0.009	–	0.029	0.079	0.066	2s(N), $2s(C_1)$, $2p_z(C_2)$
$12a_1$	−0.832	–	0.014	0.019	0.038	0.031	2s(N), 3s(Cl), $2p_z(C_2)$, $2s(C_1)$
$5b_1$	−0.860	–	0.017	–	–	–	3s(Cl), $2p_x(Be)$
$11a_1$	−0.900	0.064	0.134	–	–	–	2s(Be), 3s(Cl), 2s(N), $2p_z(N)$
$6b_2$	−1.158	–	–	0.021	0.254	0.054	$2s(C_1)$, $2s(C_2)$
$10a_1$	−1.159	–	–	0.020	0.254	0.054	$2s(C_1)$, $2s(C_2)$
$5b_2$	−1.396	–	–	0.395	0.011	–	2s(N), $2s(C_1)$
$9a_1$	−1.405	–	–	0.408	0.011	–	2s(N), $2s(C_1)$
$8a_1$	−4.716	–	–	–	–	–	1s(Be)
$7a_1$	−7.614	–	–	–	–	–	$2p_z(Cl)$
$4b_2$	−7.615	–	–	–	–	–	$2p_y(Cl)$
$1a_2$	−7.615	–	–	–	–	–	$2p_y(Cl)$
$4b_1$	−7.615	–	–	–	–	–	$2p_x(Cl)$, $2p_z(Cl)$
$3b_1$	−7.617	–	–	–	–	–	$2p_x(Cl)$, $2p_z(Cl)$
$6a_1$	−7.618	–	–	–	–	–	$2p_x(Cl)$, $2p_z(Cl)$
$2b_1$	−9.916	–	–	–	–	–	2s(Cl)
$5a_1$	−9.920	–	–	–	–	–	2s(Cl)
$4a_1$	−11.514	–	–	–	–	–	$1s(C_2)$
$3b_2$	−11.514	–	–	–	–	–	$1s(C_2)$
$2b_2$	−11.599	–	–	–	–	–	$1s(C_1)$
$3a_1$	−11.599	–	–	–	–	–	$1s(C_1)$
$1b_2$	−15.781	–	–	–	–	–	1s(N)
$2a_1$	−15.781	–	–	–	–	–	1s(N)
$1b_1$	−104.004	–	–	–	–	–	1s(Cl)
$1a_1$	−104.005	–	–	–	–	–	1s(Cl)

The structure of this ground state is closely similar to that calculated by *ab initio*. Thus, the last occupied MO's are specific for the chlorine atoms, followed by MO's which correspond exclusively to the nitrile ligands. As in the preceding case with free beryllium chloride, it is seen that the CNDO/2 calculation overestimates the role played by the beryllium 2p orbitals. However, the main difference between the electronic structures calculated by the two methods (Table XI) lies in the description of the coordinate bonds formed by the nitrile ligands with the beryllium atom.

In *ab initio*, the formation of these coordinate linkages corresponds to a transfer of 0.25 e from each nitrogen atom to the beryllium. The overlap population in the Be–N bonds is then 0.07 e. The contributions of the nitrogen 2s and $2p_\sigma$ orbitals to this transfer are practically equivalent (0.10 and 0.15 e, respectively). The charge on the nitrile carbon atoms of the methyl cyanide ligands increases from 0.10 e in the free compound to 0.23 e in the complex, owing to the fact that coordination of the nitrogen atom is accompanied by a transfer of 0.19 e along the N–C_1–C_2 π bond system

TABLE XI. Calculated Electronic Structure of $BeCl_2(NCCH_3)_2$ and $BeCl_2(NCCl)_2$.

		$BeCl_2(NCCH_3)_2$ by *ab initio*	$BeCl_2(NCCH_3)_2$ by CNDO/2	$BeCl_2(NCCl)_2$ by CNDO/2
	2s	0.468	0.563	0.577
	$2p_x$	0.129	0.774	0.785
Be	$2p_y$	0.061	0.465	0.462
	$2p_z$	0.089	0.581	0.592
	q	1.28	–0.38	–0.42
	3s	1.938	1.890	1.891
	3px	1.844	1.252	1.204
	$3p_y$	1.992	1.974	1.968
Cl_1	$3p_z$	1.933	1.837	1.846
	$3d_z^2$	–	0.018	0.021
	$3d_{xz}$	–	0.130	0.122
	$3d_{yz}$	–	0.011	0.010
	$3d_{x^2-y^2}$	–	0.125	0.129
	$3d_{xy}$	–	0.016	0.015
	q	–0.69	–0.25	–0.21
	2s	1.597	1.322	1.339
	$2p_x$	1.117	1.092	1.048
N_1	$2p_y$	1.315	1.247	1.242
	$2p_z$	1.306	1.181	1.137
	q	–0.33	0.16	0.23
	2s	0.911	1.074	1.091
	$2p_x$	0.919	0.949	0.959
C_1	$2p_y$	0.965	0.937	0.945
	$2p_z$	0.980	0.891	0.900
	q	0.23	0.15	0.11
	2s	1.238	1.003	–
	$2p_x$	1.238	1.007	–
C_2	$2p_y$	1.131	1.010	–
	$2p_z$	1.082	1.008	–
	q	–0.68	–0.03	–
	3s	–	–	1.894
	$3p_x$	–	–	1.952
	$3p_y$	–	–	1.074
	$3p_z$	–	–	1.651
	$3d_z^2$	–	–	0.033
Cl_3	$3d_{xz}$	–	–	0.017
	$3d_{yz}$	–	–	0.144
	$3d_{x^2-y^2}$	–	–	0.105
	$3d_{xy}$	–	–	0.048
	q	–	–	0.08
H_1	1s	0.717(0.727)	0.939(0.946)	–
(H_2)	q	0.28 (0.27)	0.06 (0.05)	–

towards the 2p orbitals of the nitrogen. Accordingly, the overlap population of the multiple C–N bond increases from 1.64 e in the non-coordinated nitrile to 1.74 e in the complex. However, this transfer in itself does not account for the gain of 0.39 e observed in the nitrogen $2p_\pi$ orbitals of the coordinated nitrile, and it must be assumed that a back-donation of the order of 0.19 e occurs from the beryllium atom towards the nitrile ligand. The calculated electron distribution pattern further indicates that the lone pair on the nitrogen atom remains essentially localized, with the result that the Be–N bond has appreciable ionic character.

In the semi-empirical model, the electron transfer from nitrogen to beryllium is approximately 0.45 e

(the resultant of 0.32 e and 0.13 e from the nitrogen 2s and $2p_\sigma$ orbitals respectively), and this is considerably higher than the transfer predicted by *ab initio*. Moreover, π-transfer from the C–N bond is practically negligible. On the other hand, the Be→N back-donation (≈0.14 e) is of the same order of magnitude as that determined by *ab initio*.

According to the *ab initio* treatment, formation of the complex is accompanied by a transfer of 0.13 e from the beryllium atom to each of the chlorine atoms in the $BeCl_2$ moiety. As a result, the charge on these halogen atoms increases from –0.56 e in non-coordinated triatomic $BeCl_2$ to –0.69 e in the complex. The overlap population of the Be–Cl bond decreases significantly on coordination, *i.e.*, 0.49 e in $BeCl_2$ as opposed to 0.37 e in the complex. An increase in the polarity of the Be–Cl bonds is also revealed by the CNDO/2 calculation. This increase both in the π character of the carbon–nitrogen triple bond and in the polarity of the metal–halogen bond following formation of the adduct are in excellent agreement with the shortening of the carbon–nitrogen bonds and the lengthening of the beryllium–chlorine bonds shown by the X-ray study of the methyl cyanide complex[11, 14, 20].

Theoretical consideration of the molecule $BeCl_2(NCCl)_2$ was limited to the CNDO/2 method. The calculated electronic structure is closely similar to that found in the same manner for the acetonitrile complex (Table XI).

Conclusion

It would appear from the foregoing study that both semi-empirical and *ab initio* molecular orbital techniques as applied to the description of simple molecular coordination complexes of the type $BeCl_2(NCR)_2$ account satisfactorily for variations in certain bonding relationships such as interatomic distances or polar character. Although it is evident that calculated values of orbital contributions and electron transfers will differ appreciably according to the method used, the differences found in the present case are seen to lie in the degree rather than in the form of the interpretation provided. A more marked discrepancy occurs between the computed and experimentally determined bond angles formed by the ligand atoms with beryllium. This is understandable from the nature of the approximations inherent in the semi-empirical method and from the fact that the molecular orbital treatment considers only the isolated molecule and necessarily neglects phenomena such as site-shifting and crystal field effects.

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