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The Crystal and Molecular Structure of Pentakis(methylisonitrile)cobalt(I) Perchlorate[1]

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The crystal and molecular structure of $[Co(CNCH_3)_5]ClO_4$ has been determined by single crystal X-ray study with full-matrix least-squares refinement using anisotropic temperature parameters for all atoms. The space group is $P3_121$ with $Z = 3$. The $[Co(CNCH_3)_5]^+$ ion has the shape of a trigonal bipyramid, slightly distorted due to intermolecular contacts. The shortness of the Co–C bonds, 1.87 ± 0.015 *vs.* a value of ~ 2.15 for a single bond, suggests Co–C bond orders of $\geqslant 1.5$. The very small deviation ($3 \pm 1.5°$) of one CNC angle from 180° is discussed in relation to the prediction of 180° for the CNC angle by a molecular orbital description of the CoCNC bonding and the much greater deviation which would seem a likely prediction of the valence bond description.

Introduction

The work reported here was undertaken for two reasons. First, pentakis(methylisonitrile)cobalt(I) perchlorate was expected to contain a five-coordinate complex cation, isoelectronic to $Fe(CO)_5$, and at the time this study began there was still uncertainty as to whether $Fe(CO)_5$ had a trigonal bipyramidal or square pyramidal structure. It has recently been shown that in the crystal at $\sim -80°$ the molecular structure is approximately trigonal bipyranidal.[2] However, there is a close relationship between the square pyramidal and the trigonal bipyramidal structures such that one can be transformed into the other by rather small angle deformations without any bond breaking and remaking processes. In particular, if one considers Berry's explanation[3] of the n.m.r. equivalence of all five fluorine atoms in PF_5 to be applicable to the observed n.m.r. equivalence[4,5] of the carbon atoms in $Fe(CO)_5$, one implicity supposes that the energy difference between the trigonal bipyramidal and square pyramidal arrangements is not very great. Therefore, it is not necessarily certain that the structure of $Fe(CO)_5$ at $-80°$ will hold for $[Co(CNCH_3)_5]^+$ in the perchlorate salt.

It should also be remarked that among the relatively few five-coordinate structures so far determined by X-ray methods, there are some, notably $Zn(O_2C_5H_7)_2 \cdot H_2O$[6] and Ni(triars)$Br_2$,[7] in which the configuration lies between the trigonal bipyramidal and square pyramidal limiting cases, although in others, *e.g.*, $[CuCl_5]^{3-}$ in $[Cr(NH_3)_6][CuCl_5]$[8] and $VO(O_2C_5H_7)_2$,[9] there is a close or even exact conformation to one of the limiting structures. Thus, the possibility of finding five-coordinate structures not closely conforming to either of the limiting ones must always be considered.

It may be noted that while a trigonal bipyramidal structure had previously been proposed for the $[Co(CNC_6H_5)_5]^+$ ion on the basis of its infrared spectrum in the C≡N stretching region,[10] more direct and unequivocal evidence is certainly to be desired.

The second reason for interest in the detailed structure of the $[Co(CNCH_3)_5]^+$ ion is that it constitutes a good example of an isonitrile complex and, while there has been much theoretical discussion of the probable similarity between metal-to-isonitrile and metal-to-CO bonding, and some infrared evidence[11] to support such reasoning, clear confirmation by structural data has been lacking. The only previous X-ray structural studies of isonitrile complexes to be published are those of Powell and his co-workers,[12,13] which are of low accuracy by present standards and the recent report by us[14] on the $[Co(CNCH_3)_5\text{–}Co(CNCH_3)_5]^{4+}$ ion, which also leaves something to be desired.

Experimental

Crystals suitable for X-ray analysis were obtained by reduction of the corresponding cobalt(II) compound, according to the method of Sacco and Freni.[15] The crystals are yellow and have a pronounced acicular habit, the needle axis corresponding to the crystallographic *c* direction. As the compound decomposes in air, it was necessary to enclose crystals in thin-walled, soft glass capillary tubes.

From zero level and first level Weissenberg and precession photographs, the crystals were found to belong to the trigonal system, with cell dimensions $a = 11.61 \pm 0.02$ Å. and $c = 10.75 \pm 0.02$ Å. The density measured by flotation in a mixture of chloroform and carbon tetrachloride was found to be 1.48 g. cm.$^{-3}$. There are thus three molecules per unit cell and the calculated

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[1] Supported by the U. S. Army Research Office.

[2] W. A. Hanson, *Acta Cryst.*, **15**, 930 (1962); J. Donohue and A. Caron, *ibid.*, **17**, 663 (1964).

[3] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); Berry proposes a TBP–SP–TBP mechanism in which the trigonal bipyramid (TBP) can rearrange with small expenditure of energy to a square pyramid (SP) which returns to a trigonal bipyramid in which the initial axial and equatorial positions will often be interchanged.

[4] F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *ibid.*, **29**, 1427 (1958).

[5] This result was later confirmed by R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962), and a similar rapid environmental averaging of F resonances has been found in numerous derivatives of PF_5 by E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963), who accept and extend Berry's hypothesis of a TBP–SP–TBP inversion mechanism to explain their results.

[6] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **16**, 748 (1963).

[7] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960); triars represents $(CH_3)_2As(CH_2)_3AsCH_3(CH_2)_3As(CH_3)_2$.

[8] M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

[9] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

[10] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[11] F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

[12] H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc.*, 799 (1945).

[13] R. Holme and H. M. Powell, *ibid.*, 719 (1957).

[14] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1495 (1964).

[15] A. Sacco and M. Freni, *Gazz. chim. ital.*, **89**, 1800 (1959).

density is 1.45 g. cm.$^{-3}$. The only systematic absences observed, $00l$ for $l \neq 3n$, indicated space groups $P3_1$, $P3_121$, or $P3_112$ (or their enantiomorphous equivalents) of which the first could be eliminated on the basis of the Laue symmetry, which is $\bar{3}$m.

Intensity data were collected by the equi-inclination Weissenberg method using Mo Kα radiation. Levels $hk0$ through $hk10$ were recorded by the multiple film technique, using an approximately cylindrical crystal of mean diameter *ca.* 0.2 mm. As the linear absorption coefficient for Mo Kα radiation is 12.5 cm.$^{-1}$ and the crystal was approximately cylindrical, the variation of absorption for reflections within any one equi-inclination level will be small and negligible ($\mu R \sim 0.13$). However, as the orders of the levels in l increase, the mean absorption will increase, since the X-ray path lengths are lengthened with increasing equi-inclination angle.

All intensities were estimated visually using a calibration wedge prepared from the same crystal. Approximately 700 independent reflections, in a spherical region of reciprocal space with $0 < \sin\theta \leqslant 0.4$, were measured; those reflections too weak to be measured were assigned a value one-half of the minimum observable value.[16] Lorentz and polarization corrections were applied graphically[17] and reflections on upper level photographs were also corrected for spot extension.[18] The levels were scaled individually to take account of the variations in absorption as mentioned earlier.

Structure Determination

A three-dimensional Patterson synthesis was first computed using the measured $|F(hkl)|^2$ values. This calculation and all subsequent Fourier summations were carried out using the program ERFR-2.[19]

While it is not possible to distinguish between space groups $P3_121$ and $P3_112$ from systematic absences, it is possible to do so from other considerations, *e.g.*, the symmetry of their respective Patterson summations, since the corresponding vector space groups are $P\bar{3}$m1 and $P\bar{3}$1m, which differ in the location of the mirror plane. The position of the mirror plane in the Patterson function (which was computed by reducing to the triclinic subgroup) indicated the crysal space group to be $P3_121$ (or $P3_121$).

Since the general position for either of these space groups is sixfold and there are only three molecules per unit cell, both the cobalt and chlorine atoms and the atoms of one of the isonitrile groups are required to lie on either of the special positions, 3(a) or 3(b), *i.e.*, on twofold axes. (In order for the methyl group to satisfy this requirement, the three hydrogen atoms would have to be disordered.) These two positions both give rise to the set of Harker peaks: $\bar{x}, x, {}^1/_3$; $\bar{x}, 2\bar{x}, {}^1/_3$; and $2x, x, {}^1/_3$. Examination of the Harker section, $P(x, y, {}^1/_3)$, revealed two sets of peaks of the above type, of almost equal height. However, consideration of the probable geometry of the cation indicated that one of the sets of vector peaks was unlikely to be due to cobalt–cobalt interactions, as they would place the cobalt atom much too near the threefold screw axis. Coordinates for the cobalt atom were accordingly derived from the other set and this atom was placed on a 3(b) position. No conclusive evidence could be drawn from the Patterson map with regard to the position of the chlorine atom which will lie on either a 3(a) or a 3(b) position. Apart from the two sets of peaks already mentioned, the Harker section, $P(x, y, {}^1/_3)$, was almost featureless, showing only a few other peaks of low intensity. An electron density map was therefore calculated, using signs given by the cobalt atom only, since it seemed that the chlorine position could not be fixed with any real certainty. Although there were a considerable number of spurious peaks present on this map, coordinates were derived for all of the light atoms of the complex cation and also for the chlorine atom. As expected from a stereochemical viewpoint, the chlorine atom lies on a 3(a) special position.

This total of eleven atoms was then used to phase a second electron density synthesis, from which positions were derived for the two independent oxygen atoms of the perchlorate ion. The shapes of the peaks were indicative of considerable anisotropic motion in these oxygen atoms. There were no extra peaks present at distances from the chlorine corresponding to the length of a Cl–O bond and hence there was no suggestion of a statistical disordering of the anion. In addition, the majority of the spurious peaks observed on the first Fourier map had disappeared and those few remaining were of low peak height. A structure factor calculation, including the two oxygen atoms and using an over-all temperature factor, B, of 4.0 Å.^{2}, gave a residual R (defined as $\Sigma\,||F_o| - |F_c||/\Sigma|F_o|$), of 0.28. Two cycles of Fourier refinement lowered the residual to 0.22, at which point full-matrix least-squares refinement was commenced.[20] Two cycles of refinement, in which the variables for the first cycle were the parameters and an over-all scale factor, and for the second cycle an isotropic thermal parameter per atom as well, were carried out, and these lowered the residual to 0.145.

At this stage, a weighting scheme was introduced into the refinement program. The weighting function was devised so that the average value of $w[|F_o| - |F|_o]^2$ for groups of increasing $|F_o|$ was constant, a condition for the estimated standard deviations to be valid. As anticipated, this function placed greatest weight on the structure factors of intermediate magnitude which, according to those reflections for which multiple measurements were available, were adjudged to be the more reliable.

In the next cycle, it was decided to treat the three atoms of the isonitrile group, previously assumed to lie on the twofold axis, as though they were, in fact, disordered about the axis, since the peaks on the electron density maps were quite elongated in a direction normal to the axis. However, after one cycle of refinement, the carbon and nitrogen atoms had moved back to the axis, while the methyl group had moved a little further away, suggesting that in the Co–C–N–CH$_3$

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(16) A. J. C. Wilson, *Acta Cryst.*, **2**, 318 (1949).

(17) W. Cochran, *J. Sci. Instr.*, **25**, 253 (1948).

(18) D. C. Phillips, *Acta Cryst.*, **9**, 819 (1956).

(19) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two and Three Dimensional Fourier Program for the IBM 709/7090," ERFR-2, 1962.

(20) C. T. Prewitt, SFLSQ-3, a full-matrix crystallographic least-squares refinement program for the IBM 709/7090, 1962.

TABLE I

ATOM POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

Atom	x/a	y/b	z/c	σ_x	σ_y	σ_z
Co	0.2455	(0.2455)	0.5000	0.0002	(0.0002)	. . .
C(1)	0.083	(0.083)	0.5000	0.002	(0.002)	. . .
N(1)	−0.015	(−0.015)	0.5000	0.001	(0.001)	. . .
C(2)	−0.140	(−0.140)	0.5000	0.003	(0.003)	. . .
C(3)	0.190	0.296	0.640	0.001	0.022	0.002
N(2)	0.157	0.330	0.725	0.001	0.001	0.001
C(4)	0.109	0.365	0.834	0.002	0.002	0.002
C(5)	0.247	0.385	0.412	0.002	0.002	0.002
N(3)	0.247	0.471	0.358	0.001	0.002	0.002
C(6)	0.231	0.570	0.292	0.002	0.002	0.003
Cl	0.4110	(0.4110)	0.0000	0.0006	(0.0006)	. . .
O(1)	0.312	0.383	0.089	0.003	0.002	0.003
O(2)	0.431	0.529	−0.063	0.001	0.001	0.002

[a] Parentheses are used to emphasize that for atoms on threefold special positions we necessarily have $y/b = x/a$ and $\sigma_y = \sigma_x$.

TABLE II

ANISOTROPIC TEMPERATURE PARAMETERS[a] AND THEIR STANDARD DEVIATIONS, ×10^3

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\sigma(\beta_{11})$	$\sigma(\beta_{22})$	$\sigma(\beta_{33})$	$\sigma(\beta_{12})$	$\sigma(\beta_{13})$	$\sigma(\beta_{23})$
Co	7.6	7.0	6.1	3.5	−0.5	−1.0	0.2	0.3	0.3	. . .	. . .	0.3
C(1)	8	12	12	6	−0.1	−0.2	2	4	3	. . .	. . .	3
N(1)	14	5	10	2	0.5	1	2	2	3	. . .	. . .	2
C(2)[b]	73	57	14	29	−20	−39	9	10	22	. . .	. . .	10
C(3)	11	11	7	7	1	2	2	2	2	1	2	1
N(2)	8	14	6	5	−1	2	1	2	2	1	1	1
C(4)	11	14	3	9	0.6	2	2	2	2	2	2	2
C(5)	15	16	6	11	−0.9	3	2	2	3	2	2	2
N(3)	25	13	8	12	−0.8	2	2	2	2	2	2	2
C(6)	44	19	15	21	0.9	6	4	4	4	3	3	3
Cl	11	13	12	6	−1	−2	0.6	0.9	1.1	. . .	. . .	0.7
O(1)	27	92	33	34	13	36	4	8	6	4	4	4
O(2)	17	17	34	6	−2	9	2	2	3	2	2	2

[a] The values quoted for Co, Cl, C(1), N(1), and N(2) are for the atoms at special positions x, 0, $^5/_6$ and x, 0, $^1/_3$, for which $\beta_{22} = 2\beta_{12}$ and $\beta_{23} = 2\beta_{13}$. [b] Not positive-definite.

group the Co–C–N portion is linear with a bend occurring at N. A further cycle was then carried out with only the methyl carbon atom disordered, and the residual fell to 0.123. In these latter cycles of refinement, the thermal parameters for the oxygen atoms in particular, and for one of the isonitrile groups, increased to high values and it therefore seemed worthwhile to continue refinement using anisotropic thermal parameters.

Before doing this, however, a three-dimensional difference Fourier summation was calculated, using only those reflections with $\sin\theta \leqslant 0.25$, in an attempt to locate the hydrogen atoms. However, there were no definite indications of these and the highest region of electron density was only 0.4 e/Å.$^{-3}$.

In the first cycle of anisotropic refinement, the methyl carbon atom was still treated as though it were disordered about the twofold axis. However, there was now an extremely high degree of correlation between the x and y coordinates of this atom (not present during isotropic refinement) which suggested that it might best be treated as though in fact it lay on the twofold axis, with the effect of the disorder, if there actually is one, being absorbed into the anisotropic thermal parameters.

A final cycle of anisotropic refinement carried out in this way produced only negligible changes in all positional parameters, indicating that convergence of these to their final values had been reached. The final unweighted residual, R, is 0.091, while the final weighted residual is 0.087. The final positional parameters and their standard deviations, computed from the least-squares formula $\sigma^2(j) = a_{jj}(\Sigma w\Delta^2)/(m - n)$ (where a_{jj} is the appropriate element of the matrix inverse to the normal equation matrix), are listed in Table I. The anisotropic thermal parameters, β_{ij}, are listed in Table II, and they represent the ijth coefficients in the expression

$$\exp -(\beta_{11}h^2 + 2\beta_{12}hk - \beta_{22}h^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl)$$

The atomic scattering factors used in this analysis were: for cobalt(I) that tabulated by Freeman and Watson[21]; for chlorine that tabulated by Dawson[22]; and for carbon, nitrogen, and oxygen those tabulated by Hoeni and Ibers.[23] The final calculated structure factors based on the parameters in Tables I and II are listed in Table III, together with the observed values. Reflection 211 was omitted from refinement as it most probably suffers from extinction.

Discussion

The internal dimensions of the $[Co(CNCH_3)_5]^+$ ion are listed in Table IV. Figure 1 is a perspective view of the ion which shows the numbering of the atoms.

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[21] A. J. Freeman and R. E. Watson, *Acta Cryst.*, **14**, 27 (1961).

[22] B. Dawson, *ibid.*, **13**, 403 (1960).

[23] J. A. Hoeni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

TABLE III

3	0	0	26.5	25.0
4	0	0	50.3	51.6
5	0	0	39.2	38.2
6	0	0	15.6	16.3
7	0	0	26.7	24.7
8	0	0	33.9	34.2
9	0	0	18.5	18.5
10	0	0	3.8	2.2
11	0	0	6.0	4.3
2	1	0	34.0	35.1
3	1	0	40.4	43.8
4	1	0	21.0	17.8
5	1	0	33.4	33.7
6	1	0	34.5	34.7
7	1	0	9.5	7.9
8	1	0	15.6	15.3
9	1	0	7.0	7.6
10	1	0	12.7	14.6
2	2	0	34.3	32.7
3	2	0	34.2	31.4
4	2	0	28.2	26.5
5	2	0	21.0	21.6
6	2	0	17.1	19.7
7	2	0	16.8	17.4
8	2	0	3.5	2.6
9	2	0	6.0	6.3
10	2	0	4.9	4.6
3	3	0	31.5	28.8
4	3	0	17.5	15.6
5	3	0	24.0	24.1
6	3	0	15.3	17.8
7	3	0	16.8	17.0
8	3	0	4.9	3.2
9	3	0	7.9	7.4
4	4	0	31.5	33.5
5	4	0	18.5	20.2
6	4	0	10.5	10.1
7	4	0	4.9	4.9
8	4	0	16.8	17.1
5	5	0	18.5	17.1
6	5	0	20.1	19.6
7	5	0	11.6	11.5
8	5	0	8.6	8.2
6	6	0	11.1	8.9
7	6	0	15.3	13.7
3	0	1	144.5	134.9
4	0	1	14.1	15.0
5	0	1	23.7	21.9
6	0	1	27.6	29.6
7	0	1	29.5	30.1
8	0	1	16.5	13.6
9	0	1	7.0	8.0
10	0	1	17.4	17.9
11	0	1	11.5	9.2
2	1	1	64.6	95.6
3	1	1	40.2	37.8
4	1	1	58.7	60.3
5	1	1	22.7	27.6
6	1	1	21.0	25.1
7	1	1	21.6	19.9
8	1	1	21.0	23.4
9	1	1	12.9	11.3
10	1	1	7.0	8.1
1	2	1	37.4	39.0
2	2	1	50.2	51.7
3	2	1	21.9	23.0
4	2	1	37.8	39.3
5	2	1	13.6	9.8
6	2	1	20.0	19.3
7	2	1	15.2	15.6
8	2	1	14.6	14.2
9	2	1	11.3	12.2
10	2	1	5.5	3.4
0	3	1	37.6	33.9
1	3	1	26.1	26.2
2	3	1	22.5	24.8
3	3	1	9.9	11.4
4	3	1	13.6	11.5
5	3	1	44.3	43.7
6	3	1	19.0	17.9
7	3	1	12.2	12.5
8	3	1	10.8	11.0
9	3	1	12.9	13.8
0	4	1	13.5	11.7
1	4	1	13.5	14.6
2	4	1	9.4	16.2
3	4	1	42.1	42.0
4	4	1	8.8	7.2
5	4	1	14.0	8.0
6	4	1	24.2	24.3
7	4	1	19.7	21.6
8	4	1	8.8	8.6
0	5	1	50.2	45.0
1	5	1	24.6	18.6
2	5	1	3.1	4.3
3	5	1	17.1	15.1
4	5	1	25.4	27.5
5	5	1	12.9	12.5
6	5	1	7.6	6.8
7	5	1	5.9	6.2
8	5	1	8.8	11.1
0	6	1	28.8	25.8
1	6	1	9.6	8.5
2	6	1	20.5	20.4
3	6	1	10.6	12.1
4	6	1	9.9	12.0
5	6	1	8.3	9.9
6	6	1	8.8	9.9
7	6	1	8.3	4.1
0	7	1	4.5	2.9
1	7	1	27.4	27.4
2	7	1	20.5	20.4
3	7	1	10.0	9.1
4	7	1	4.4	2.9
5	7	1	11.3	11.0
6	7	1	12.9	11.2
0	8	1	15.0	12.0
1	8	1	13.6	11.3
2	8	1	20.2	19.5
3	8	1	19.2	18.7
4	8	1	3.2	1.0
5	8	1	7.6	6.4
0	9	1	21.2	23.6
1	9	1	17.4	18.1
2	9	1	4.4	6.7
3	9	1	8.3	8.9
0	10	1	7.0	5.9
1	10	1	7.0	8.1
2	10	1	7.0	9.1
3	0	2	8.2	10.2
4	0	2	13.7	16.9
5	0	2	55.2	51.3
6	0	2	65.7	67.4
7	0	2	19.6	19.9
8	0	2	10.3	9.9
9	0	2	12.0	14.7
10	0	2	12.8	15.8
2	1	2	47.6	50.5
3	1	2	44.6	43.7
4	1	2	32.0	33.3
5	1	2	41.7	41.6
6	1	2	10.3	12.2
7	1	2	34.8	35.4
8	1	2	12.0	17.0
9	1	2	8.8	8.8
10	1	2	7.6	.7
1	2	2	63.7	58.6
2	2	2	49.9	49.3
3	2	2	16.8	16.4
4	2	2	21.3	19.9
5	2	2	34.8	37.9
6	2	2	22.8	22.1
7	2	2	12.7	13.2
8	2	2	9.8	8.0
9	2	2	13.9	14.3
0	3	2	55.8	50.5
1	3	2	42.4	39.5
2	3	2	20.1	19.1
3	3	2	26.1	27.9
4	3	2	16.8	18.7
5	3	2	8.2	8.7
6	3	2	9.8	9.8
7	3	2	11.2	10.8
8	3	2	18.9	19.8
9	3	2	4.4	5.4
0	4	2	28.2	28.4
1	4	2	49.8	50.5
2	4	2	18.9	23.6
3	4	2	12.1	14.5
4	4	2	8.2	8.4
5	4	2	11.6	14.5
6	4	2	14.9	17.0
7	4	2	7.0	5.8
8	4	2	7.6	5.6
0	5	2	17.4	15.2
1	5	2	18.6	20.8
2	5	2	21.1	19.8
3	5	2	18.6	19.2
4	5	2	6.2	5.4
5	5	2	10.3	10.0
6	5	2	10.8	11.4
7	5	2	15.8	16.8
0	6	2	40.0	42.5
1	6	2	21.8	22.0
2	6	2	31.5	32.2
3	6	2	17.3	15.7
4	6	2	12.0	15.0
5	6	2	12.4	14.1
6	6	2	12.8	14.6
0	7	2	42.5	44.1
1	7	2	19.1	20.1
2	7	2	7.0	8.5
3	7	2	10.3	10.7
4	7	2	19.1	20.3
5	7	2	11.2	10.4
0	8	2	7.6	6.1
1	8	2	18.4	17.7
2	8	2	11.2	10.9
3	8	2	4.4	.6
4	8	2	7.6	8.7
0	9	2	4.4	3.4
1	9	2	11.2	10.5
2	9	2	3.1	1.3
3	9	2	12.0	11.6
0	10	2	11.2	8.8
1	10	2	11.6	8.0
3	0	3	3.5	1.6
4	0	3	53.9	53.7
5	0	3	3.5	4.3
6	0	3	6.0	6.8
7	0	3	3.5	4.3
8	0	3	42.4	42.5
9	0	3	13.9	13.3
10	0	3	9.2	9.8
2	1	3	63.9	64.3
3	1	3	22.8	26.6
4	1	3	42.8	41.8
5	1	3	29.3	31.7
6	1	3	25.3	25.9
7	1	3	21.5	20.6
8	1	3	22.5	20.9
9	1	3	8.7	8.1
10	1	3	9.2	8.3
1	2	3	31.2	34.9
2	2	3	25.3	30.6
3	2	3	47.5	44.0
4	2	3	19.7	21.1
5	2	3	35.6	37.1
6	2	3	13.0	11.8
7	2	3	14.6	17.2
8	2	3	13.0	10.0
9	2	3	12.5	11.6
0	3	3	81.1	73.0
1	3	3	34.8	39.3
2	3	3	45.2	38.3
3	3	3	50.3	52.0
4	3	3	23.3	21.6
5	3	3	3.5	1.8
6	3	3	23.0	24.1
7	3	3	17.0	15.6
8	3	3	12.5	10.1
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1	4	3	38.2	43.3
2	4	3	9.8	14.2
3	4	3	12.5	13.6
4	4	3	38.0	36.0
5	4	3	15.1	16.2
6	4	3	6.9	6.1
7	4	3	7.8	7.9
8	4	3	9.2	10.5
0	5	3	13.0	12.0
1	5	3	16.7	17.3
2	5	3	33.1	32.0
3	5	3	13.9	12.6
4	5	3	9.0	7.8
5	5	3	17.4	15.2
6	5	3	16.3	12.9
7	5	3	4.9	4.3
0	6	3	3.5	6.2
1	6	3	20.6	19.6
2	6	3	11.0	8.7
3	6	3	14.7	17.3
4	6	3	7.8	6.7
5	6	3	12.0	12.1
6	6	3	8.5	2.6
0	7	3	3.5	3.1
1	7	3	14.3	12.5
2	7	3	11.5	10.5
3	7	3	21.7	20.4
4	7	3	4.9	5.9
0	8	3	21.1	22.1
1	8	3	26.2	22.9
2	8	3	4.9	5.6
3	8	3	11.5	10.9
4	8	3	13.9	15.3
0	9	3	7.8	7.0
1	9	3	9.7	9.0
2	9	3	17.0	16.2
3	9	3	4.9	6.1
0	10	3	7.8	8.0
1	10	3	9.2	7.6
3	0	4	52.2	49.0
4	0	4	24.6	24.9
5	0	4	3.3	3.1
6	0	4	28.0	29.1
7	0	4	33.2	35.1
8	0	4	4.7	.1
9	0	4	3.3	3.3
10	0	4	4.7	6.1
2	1	4	33.6	32.2
3	1	4	17.9	18.3
4	1	4	10.5	10.0
5	1	4	33.5	35.0
6	1	4	20.9	22.1
7	1	4	14.8	17.1
8	1	4	11.0	11.6
9	1	4	12.0	12.3
10	1	4	8.8	8.6
1	2	4	21.8	21.2
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3	2	4	26.5	28.6
4	2	4	30.6	31.6
5	2	4	22.3	20.6
6	2	4	22.6	21.5
7	2	4	9.7	11.2
8	2	4	8.8	10.0
9	2	4	4.7	2.6
0	3	4	3.3	8.5
1	3	4	46.5	45.2
2	3	4	14.5	12.3
3	3	4	32.8	32.8
4	3	4	3.3	5.5
5	3	4	29.6	28.4
6	3	4	15.5	16.5
7	3	4	12.4	13.2
8	3	4	3.3	4.1
0	4	4	10.0	7.5
1	4	4	34.9	35.8
2	4	4	36.0	38.4
3	4	4	32.7	32.6
4	4	4	5.8	3.4
5	4	4	4.7	6.1
6	4	4	8.1	6.9
7	4	4	12.8	13.3
0	5	4	60.9	60.2
1	5	4	21.5	18.7
2	5	4	28.1	29.8
3	5	4	13.3	12.5
4	5	4	19.6	21.2
5	5	4	4.7	7.8
6	5	4	12.4	12.7
7	5	4	4.7	3.9
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1	6	4	27.5	25.5
2	6	4	13.3	14.9
3	6	4	14.1	16.7
4	6	4	16.9	17.4
5	6	4	4.7	5.2
6	6	4	13.7	13.8
0	7	4	3.3	1.7
1	7	4	25.3	23.5
2	7	4	14.5	13.9
3	7	4	11.5	8.6
4	7	4	4.7	6.2
5	7	4	12.8	12.6
0	8	4	3.3	3.7
1	8	4	3.3	.4
2	8	4	10.3	8.5
3	8	4	14.8	15.5
0	9	4	11.5	12.3
1	9	4	4.7	4.7
2	9	4	11.0	10.3
0	10	4	12.4	12.8
1	10	4	4.7	5.3
3	0	5	7.4	7.6
4	0	5	7.4	3.8
5	0	5	36.3	33.1
6	0	5	9.0	7.4
7	0	5	0.	.4
8	0	5	7.4	7.8
9	0	5	11.1	12.4
10	0	5	11.6	10.0
2	1	5	12.2	17.9
3	1	5	42.7	42.7
4	1	5	14.7	12.3
5	1	5	27.6	24.5
6	1	5	5.2	3.7
7	1	5	8.3	7.2
8	1	5	7.4	5.8
9	1	5	9.8	10.1
1	2	5	34.8	31.7
2	2	5	21.2	20.5
3	2	5	26.3	25.9
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5	2	5	3.7	2.2
6	2	5	17.3	16.2
7	2	5	16.1	16.0
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5	4	5	20.5	22.5
6	4	5	12.7	12.6
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1	6	5	19.5	21.4
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5	6	5	8.3	4.8
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2	7	5	9.0	10.1
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1	8	5	11.6	12.4
2	8	5	14.7	14.3
3	8	5	5.2	6.7
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1	9	5	10.4	8.4
2	9	5	5.2	5.3
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6	0	6	19.9	21.1
7	0	6	12.9	12.1
8	0	6	14.3	16.3
9	0	6	12.9	10.8
2	1	6	21.7	26.1
3	1	6	24.2	26.0
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5	1	6	16.4	19.4
6	1	6	15.6	14.0
7	1	6	3.6	2.6
8	1	6	9.5	9.3
9	1	6	6.2	4.4
1	2	6	23.1	23.5
2	2	6	11.9	12.0
3	2	6	33.3	30.5
4	2	6	15.1	14.7
5	2	6	16.8	18.9
6	2	6	5.0	2.5
7	2	6	8.0	8.3
8	2	6	5.0	3.8
0	3	6	11.3	11.0
1	3	6	19.3	21.1
2	3	6	30.9	28.5
3	3	6	18.2	18.3
4	3	6	11.3	11.5
5	3	6	12.4	14.1
6	3	6	8.0	9.6
7	3	6	12.4	14.6
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2	4	6	17.9	15.9
3	4	6	16.8	18.0
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6	4	6	12.9	10.2
7	4	6	9.5	6.6
8	4	6	14.7	15.1
9	4	6	8.8	6.9
10	4	6	9.5	1.5
0	5	6	29.7	28.8
1	5	6	27.2	27.1
2	5	6	17.1	19.6
3	5	6	6.2	6.0
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5	5	6	13.4	15.9
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0	6	6	9.5	10.6
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1	7	6	8.8	8.8
2	7	6	8.8	10.0
3	7	6	11.9	12.0
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1	8	6	8.8	8.4
2	8	6	8.8	8.6
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1	9	6	8.0	6.7
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4	0	7	11.9	12.9
5	0	7	7.4	6.5
6	0	7	11.1	12.0
7	0	7	13.9	16.0
8	0	7	6.9	5.4
9	0	7	8.3	7.0
2	1	7	26.5	26.7
3	1	7	12.9	13.5
4	1	7	25.5	27.0
5	1	7	7.4	7.7
6	1	7	8.3	9.6
7	1	7	13.9	12.1
8	1	7	11.7	11.3
1	2	7	16.2	20.4
2	2	7	26.3	26.3
3	2	7	12.9	16.6
4	2	7	14.4	13.4
5	2	7	3.7	3.0
6	2	7	11.1	11.3
7	2	7	7.4	4.8
0	3	7	16.2	14.6
1	3	7	41.5	41.1
2	3	7	18.6	18.7
3	3	7	13.8	13.2
4	3	7	3.7	5.3
5	3	7	22.3	21.9
6	3	7	12.9	11.2
7	3	7	9.1	6.0
0	4	7	9.1	8.6
1	4	7	11.9	7.4
2	4	7	7.4	9.3
3	4	7	20.7	19.8
4	4	7	3.7	6.0
5	4	7	3.7	2.4
6	4	7	12.2	11.0
0	5	7	33.7	33.6
1	5	7	20.0	19.9
2	5	7	8.9	9.9
3	5	7	8.3	7.6
4	5	7	19.3	17.6
5	5	7	7.4	6.5
0	6	7	7.4	4.8
1	6	7	9.1	8.7
2	6	7	16.6	17.3
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2	7	7	9.1	12.4
3	7	7	13.4	11.8
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1	8	7	13.4	13.5
0	9	7	9.1	13.2
3	0	8	4.1	4.5
4	0	8	4.1	5.5
5	0	8	31.2	32.1
6	0	8	22.4	23.0
7	0	8	9.2	6.8
8	0	8	10.0	1.0
2	1	8	11.6	12.9
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5	1	8	8.2	8.8
6	1	8	10.0	10.3
7	1	8	16.4	15.5
1	2	8	12.9	12.0
2	2	8	11.6	15.3
3	2	8	7.1	6.2
4	2	8	15.8	16.9
5	2	8	12.9	13.5
6	2	8	8.2	9.8
7	2	8	10.0	10.8
0	3	8	35.2	34.5
1	3	8	5.8	3.2
2	3	8	18.7	19.5
3	3	8	11.6	13.3
4	3	8	17.8	18.8
5	3	8	9.2	9.8
6	3	8	5.8	6.0
0	4	8	21.3	20.1
1	4	8	21.3	20.6
2	4	8	14.1	16.8
3	4	8	8.2	7.5
4	4	8	9.2	5.1
5	4	8	10.0	11.7
0	5	8	8.2	7.9
1	5	8	17.8	15.7
2	5	8	7.1	6.3
3	5	8	15.8	16.8
4	5	8	10.0	8.0
0	6	8	12.9	12.0
1	6	8	9.2	7.8
2	6	8	14.1	12.6
3	6	8	8.2	5.5
0	7	8	14.1	10.7
1	7	8	9.2	6.0
2	7	8	5.8	2.0
0	8	8	10.0	5.6
3	0	9	4.0	2.2
4	0	9	22.5	24.3
5	0	9	4.0	1.8
6	0	9	8.1	1.5
7	0	9	0.	.5
2	1	9	14.6	18.8
3	1	9	22.6	24.2
4	1	9	8.1	6.6
5	1	9	14.0	12.5
6	1	9	9.9	12.0
1	2	9	25.2	23.3
2	2	9	4.0	4.3
3	2	9	16.6	16.7
4	2	9	4.1	4.2
5	2	9	9.9	11.7
6	2	9	9.0	9.6
0	3	9	9.9	9.6
1	3	9	10.7	9.9
2	3	9	19.8	18.2
3	3	9	22.9	22.5
4	3	9	9.9	9.2
5	3	9	9.0	6.8
0	4	9	12.9	12.7
1	4	9	8.1	10.0
2	4	9	5.6	4.8
3	4	9	4.0	1.4
4	4	9	18.1	19.7
0	5	9	0.	.5
1	5	9	9.9	8.5
2	5	9	15.1	13.2
3	5	9	4.1	4.4
0	6	9	5.7	4.4
1	6	9	9.0	6.4
2	6	9	7.0	5.7
0	7	9	4.1	1.8
3	0	10	23.8	25.2
4	0	10	4.5	2.2
5	0	10	7.8	7.4
6	0	10	13.5	13.4
2	1	10	11.0	12.5
3	1	10	4.5	1.8
4	1	10	12.7	13.6
5	1	10	14.9	16.7
1	2	10	14.9	17.0
2	2	10	7.8	4.4
3	2	10	11.9	9.3
4	2	10	13.5	13.6
0	3	10	8.5	8.7
1	3	10	9.0	7.7
2	3	10	9.0	6.4
3	3	10	7.8	7.8
0	4	10	4.5	3.0
1	4	10	5.7	4.7
2	4	10	7.8	8.2
0	5	10	10.5	10.9
1	5	10	8.1	8.8
0	6	10	20.1	16.8

TABLE IV

INTERNAL DIMENSIONS[a] OF THE $[Co(CNCH_3)_5]^+$ ION

Bond distances, Å.		Interbond angles, deg.		Intramolecular nonbonded contact distances, Å.	
Co–C(1)	1.88 ± 0.02	Co–C(1)–N(1)	180.00[c]	C(1)–C(3)	2.62 ± 0.03
Co–C(5)	1.88 ± 0.02	Co–C(3)–N(2)	179 ± 1.3	C(3)–C(5)	2.51 ± 0.03
Co–C(3)	1.84 ± 0.02	Co–C(5)–N(3)	180 ± 1.5	C(3)–C(5)′	2.66 ± 0.03
C(1)–N(1)	1.14 ± 0.03	C(1)–Co–C(3)	89.2 ± 0.6	C(1)–C(5)	3.19 ± 0.03
C(3)–N(2)	1.14 ± 0.02	C(3)–Co–C(5)	89.3 ± 0.7	C(5)–C(5)′	3.40 ± 0.03
C(5)–N(3)	1.15 ± 0.03	C(3)–Co–C(5)′	91.4 ± 0.8		
N(2)–C(4)	1.44 ± 0.02	C(1)–Co–C(5)	115.9 ± 0.7		
N(3)–C(6)	1.44 ± 0.03	C(5)–Co–C(5)′	128.3 ± 0.8		
N(1)–C(2)	1.45 ± 0.04[b]	C(3)–N(2)–C(4)	177 ± 1.5		
		C(5)–N(3)–C(6)	173 ± 2.0		
		C(3)–Co–C(3)′	180.00[c]		

[a] The intervals are standard deviations, derived from the standard deviations in the atom coordinates of Table I. [b] For reasons discussed in the text, this dimension and its standard deviation should not be accepted uncritically. [c] By symmetry due to the twofold axis.

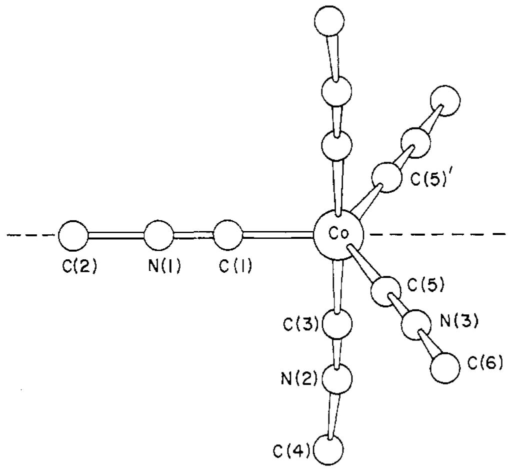

Figure 1.—Perspective view of the complex cation [Co-$(CNCH_3)_5]^+$ with the atoms numbered as in Tables I, II, and IV.

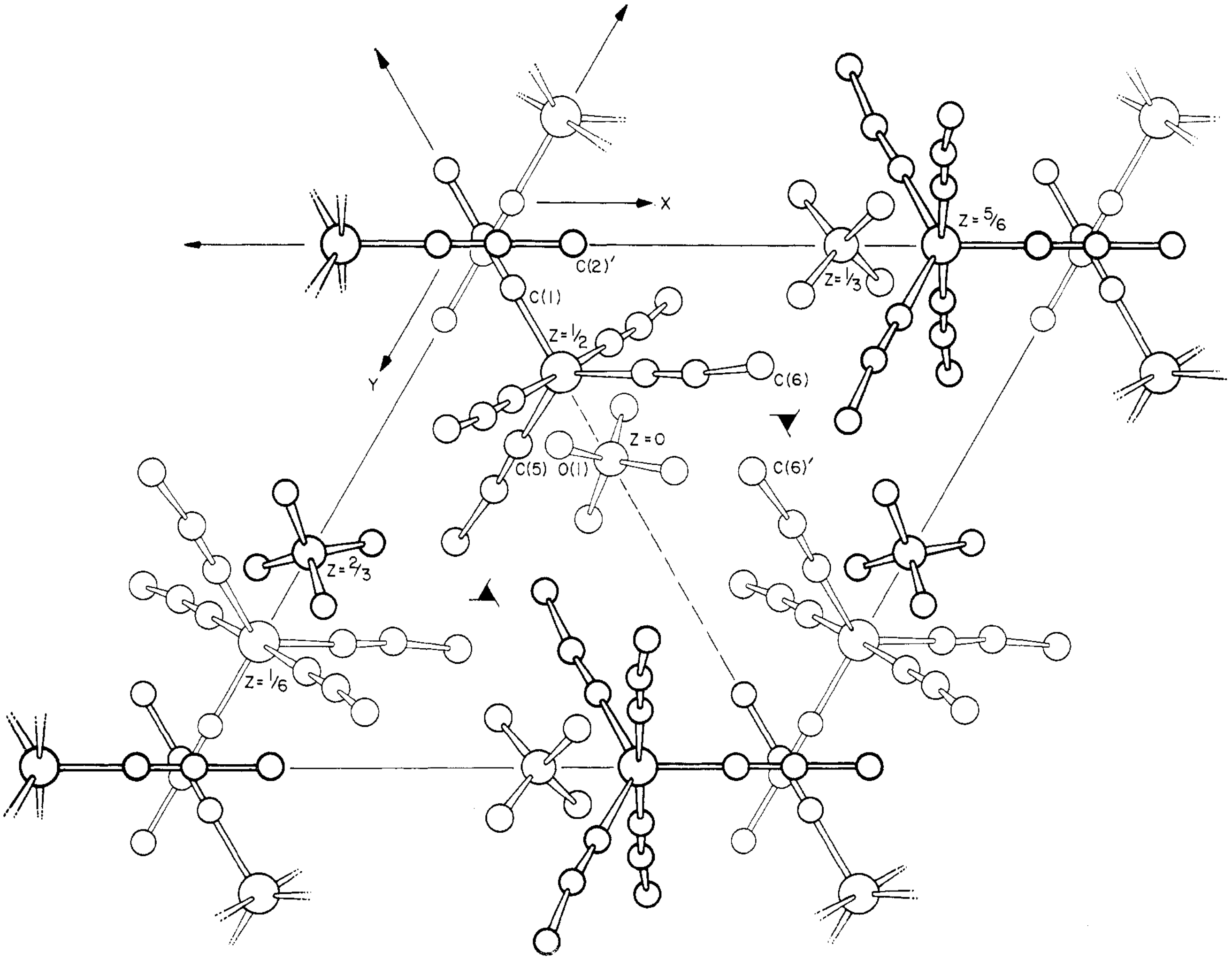

Figure 2.—The contents of one unit cell projected onto (001). Closest intermolecular distances between atoms indicated are C(1)–C(2)', 3.68 Å.; O(1)–C(5), 3.62 Å.; C(4)–C(2)', 4.18 Å.; and C(6)–C(6)', 4.11 Å.

Coordination Polyhedron about the Cobalt.—The data in Table IV show that the coordination polyhedron about Co is a trigonal bipyramid, slightly distorted by intermolecular interactions. This conclusion rests on a comparison of the observed values of the nine C–Co–C angles with the values expected, *viz.*, six of them 90° and three 120°, for a perfect trigonal bipyramid. It may first be noted that the only symmetry element of a trigonal bipyramid which exists here by virtue of the crystallographic symmetry requirements is the twofold axis through Co, C(1), and N(1). Two important consequences of this are (1) the C(3)–Co–C(3)' group must be linear, and (2) the Co–C(1), Co–C(5), and Co–C(5)' bonds must all be coplanar.

From Table IV it may be seen that the six angles between the C(3)–Co–C(3)' group and the set of three Co–C bonds which would define the equatorial plane of a trigonal bipyramid are all within less than two standard deviations of 90°, which means that they do not differ significantly from that value, which is the expected one for a true trigonal bipyramid.

It is only for the C–Co–C angles in the equatorial plane that there appear to be deviations from the ideal angles (120°) which are large enough to be considered as definitely real. Thus, for the C(1)–Co–C(5) angle, 115.9 ± 0.7°, we have $\Delta/\sigma = 6.8$ and for the C(5)–Co–C(5)' angle, 128.3 ± 0.8°, we have $\Delta/\sigma = 10.4$. However, it appears that these deviations are direct

TABLE V

DIMENSIONS OF THE PERCHLORATE ION

Cl–O(1), Å.	1.41 ± 0.03	Cl–O(2), Å.	1.44 ± 0.02
O(1)–Cl–O(1)′, deg.	116.9 ± 1.5	O(1)–Cl–O(2), deg.	105.0 ± 1.5
O(2)–Cl–O(2)′, deg.	112.4 ± 0.9	O(1)–Cl–O(2)′, deg.	108.5 ± 1.4

consequences of intermolecular forces. This can best be seen in Figure 2. The $[Co(CNCH_3)_5]^+$ ions are arranged in a rather tight spiral around the threefold screw axis, so that C(6) atoms of one ion contact those of the others; every C(6), and the CNC chain of which it is the terminal member, tends to be pushed away from the screw axis by the corresponding parts of other molecules. The distance from C(6) in one molecule to C(6)′ in another is 4.11 Å., which is approximately twice the van der Waals radius of a methyl group (2.0 Å.[24]). However, if the C(5)–Co–C(5)′ angle were contracted to 120°, the C(6)–C(6)′ intermolecular distance would drop to about 3.75 Å., which is appreciably shorter than the sum of the van der Waals radii. Since the force constant for C–Co–C bending is presumably very low (in metal carbonyls such constants are typically very small, *viz.*, ~0.2 mdyne/Å.[25]) small changes in the relevant C–Co–C angles apparently afford a satisfactory way to minimize the intermolecular repulsion forces.

The Perchlorate Ions.—The dimensions of the perchlorate ions are all reasonable, but little more can be said of them on account of the rather large standard deviations in the dimensions and the large values of the temperature parameters of the oxygen atoms. Each perchlorate ion lies with a twofold axis of the idealized tetrahedron coincident with a crystallographic twofold axis (see Figure 2). The nonequivalent Cl–O bond distances and O–Cl–O bond angles are given in Table V. The two angles, O(1)–Cl–O(1)′ and O(2)–Cl–O(2)′, which are bisected by the twofold axis, have a mean value of 114.7° with a standard deviation of the mean (σ_m) of 1.2°, whereas the mean of the other four angles is 106.8° with a σ_m of 1.4°. However, it is not necessarily certain that the tetrahedron is significantly flattened since $\Delta/\Sigma\sigma_m$ is only 3.0 and the large temperature parameters for the oxygen atoms probably lessen the confidence one can place in the usual statistical test of significance, according to which a Δ/σ ratio of 3 would be just at the threshold of significance.

The Cl–O distances do not differ significantly, having a mean value of 1.425 Å. with σ_m = 0.018 Å., which agrees with the accepted value[26] of 1.44 Å. In all probability the Cl–O(1) distance found is too short since it is the O(1) atoms which are undergoing large-amplitude vibration judging by their temperature parameters (Table II). Therefore an unusually large "shortening" effect would be expected for the Cl–O(1) bonds.

Metal-to-Ligand π-Bonding.—The structural data obtained in this study offer the opportunity to check on the *existence* of metal-to-ligand multiple bonding and to estimate, at least roughly, the *extent* to which it occurs. They also afford an opportunity to test the merits of the valence bond and molecular orbital formulations of this bonding since the two theories make different predictions regarding structure.

The present structural data unequivocally support the view that appreciable metal-to-ligand $d\pi \rightarrow p\pi$ back bonding occurs in $[Co(CNCH_3)_5]^+$. Strong evidence for this comes from the Co–C bond lengths. All three crystallographically nonequivalent ones are equal within the limits of significance of the data, and in subsequent discussion the mean, 1.87 ± 0.015 Å., will be used. As indicated in a previous paper,[14] the Co–C single bond distance is expected to be around 2.15 Å., and certainly not less than 2.00. Thus, the observed bond lengths are at least 0.13 Å. shorter and probably 0.25–0.30 Å. shorter than the single bond distance. To the previous arguments indicating a Co–C single bond distance of 2.15 Å. may be added Pauling's estimate[27] of 2.16 Å. for a Ni–C bond. The shortening in the present case is quite similar to that in $Ni(CO)_4$ (Ni–C, 1.82 ± 0.03 Å.), which is generally believed[27] to have extensive Ni–C multiple bonding, with bond orders perhaps in the neighborhood of 1.75[28] according to a valence bond theory treatment.

The principle of electroneutrality would of course favor an appreciable amount of back bonding. To keep the net charge on Co in $[Co(CNCH_3)_5]^+$ between 0 and +1, the number of electron pairs back-donated from Co to each C would have to be in the range $^4/_5$ to 1, giving Co–C bond orders in the range 1.8 to 2.0.

Finally, by comparison with some structural data now available for *cis*-dienMo$(CO)_3$, the degree of Co–C multiple bonding can be estimated in another way. For *cis*-dienMo$(CO)_3$, it has been found[29] that the Mo–C distances are 1.95 ± 0.015 Å. This is 0.13 ± 0.06 Å. shorter than the Mo–C distance, 2.08 ± 0.04 Å., in $Mo(CO)_6$.[30] Now, according to arguments recently presented,[31] on the basis of vibrational data, the Mo–C bond orders increase by approximately 0.5, that is by one-half electron pair per bond, on going from $Mo(CO)_6$ to *cis*-dienMo$(CO)_3$. Thus, if the contraction of 0.13 Å. in a Mo–C bond per 0.5 increase in Mo–C bond order is taken to apply, at least approximately, for a Co–C bond, we may say that a contraction in the latter of 0.13–0.25 Å. corresponds to an increase in Co–C bond order of 0.5–1.0, thus leading to the conclusion that the bond order of the Co–C bonds in $[Co(CNCH_3)_5]^+$ is at least 1.5 and probably greater.

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[24] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.

[25] L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962).

[26] Reference 24, Table 9-2, p. 321.

[27] Reference 24, p. 332.

[28] G. Giacometti, *J. Chem. Phys.*, **23**, 2068 (1955).

[29] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965); dien = diethylenetriamine.

[30] L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

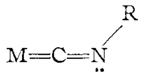
[31] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

It might, at first thought, be supposed that the Co to C multiple bonding would also be evidenced by a lengthening of the C≡N bond. No lengthening can be said to occur, however, since the mean of the distances found, 1.14 ± 0.02 Å., is insignificantly different from the C≡N distances in CH_3—N≡C itself,[32] 1.166 Å. This result should not actually be considered surprising or inconsistent, as will now be shown. First, for metal carbonyls, the C–O bond lengths[33] are always found to be in the range 1.14–1.16 Å., with an uncertainty in any individual one of about 0.02 Å.; that is, they are not significantly greater than the bond length in CO itself (1.13 Å.). This, in turn, fits in well with the apparently general insensitivity of C—O bond lengths to bond order, in the range 2–3, provided the hybridization of carbon is kept fixed. Thus the C═O bonds in CO_2, COS, COSe, HN═C═O, CH_3N═C═O, and CH_2═C═O are all about 1.165 Å. compared to 1.13 Å. in C≡O. While comparably extensive data are unavailable for C═N compounds, it seems reasonable to expect a similar insensitivity. The particular cases of CH_3N═C═O (1.16 ± 0.02 Å) and R^1R^2C═C═N—CH_3 (1.15 ± 0.02 Å.) provide rather direct evidence that this is so.

We now take up the question of how best to describe the electronic structure of an entire MCNC or MCO group, when the MC bonds have appreciable π-character. For the isonitrile compounds we may consider first a valence bond (resonance) description, in which the true electron distribution is taken to be an appropriately weighted hybrid[34] of I and II. For MCO groups the analogous description uses I′ and II′.

$\mathrm{M{-}C{\equiv}N{-}R}$

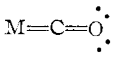
I



II

$\mathrm{M{-}C{\equiv}O}$

I′



II′

Alternatively, from a molecular orbital viewpoint, one may consider that the back-donated dπ electrons enter π-antibonding CN or CO orbitals. For the MCO case, it is difficult if not impossible to devise any experimental measurements which can distinguish between these alternative descriptions, and therefore, from a positivistic viewpoint, they might be accepted as equally valid.

However, for isonitrile compounds, an experimentally detectable distinction exists. In the resonance description, I ↔ II, a bent MCNC chain is expected, the bend at the N atom increasing with increasing π-character in the MC bond, whereas in the molecular orbital description no deviation from complete linearity is to be expected. The present data appear to be the first ones for an isonitrile complex which are accurate enough to provide a basis for at least a tentative decision between the alternative descriptions of the bonding.

There are three crystallographically distinct Co–CNC chains in the $[Co(CNCN_3)_5]^+$ ion. We have already discussed the probable occurrence of distortion in the Co–C(5)–N(3)–C(6) chain due to intermolecular contacts; this one therefore is clearly not suitable for a discussion of the "inherent" structure of the chain. The Co–C(1)–N(1)–C(2) chain is also unsuitable because of uncertainty about its structure. As explained in the Experimental section there may be a small bend at N(1) with disordering of C(2) about the crystallographic axis or this chain may be linear with the C(3) methyl group having a very large thermal motion. It is not possible to state with certainty which of these possibilities is correct. Although the latter one served better in handling the refinement, this does not prove it to be correct, and against this is the fact that during an earlier refinement with isotropic temperature factors C(3) failed to move back to the twofold axis when it was initially placed ~0.05 Å. off of it. This leaves then the Co–C(3)–N(2)–C(4) chain, which does not appear to be subject to any unusual uncertainties nor to any obvious intermolecular distorting forces.

Taking, then, the result for the axial CoCNC chains as apparently unambiguous, we ask how the observed CNC angle of 177 ± 1.5° tallies with the values expected from the valence bond and MO descriptions. Obviously, this value does not differ significantly ($\Delta/\sigma < 3$) from 180°; it therefore agrees well with MO theory. The apparent though not necessarily real deviation of 3° from 180° could—if real—be caused by slight intermolecular forces in the crystal.

To be as thorough as possible, let us assume that there is actually a bend of at least 3° and perhaps as much as $3° + 4\sigma$, namely 9°, since this is not entirely impossible (though unlikely) on the basis of considerations of the statistical significance of the results. We then need to ask whether a bend of 9° might be considered to satisfy the valence bond description. The answer can only be given if a relationship between the CNC angle, or its supplement which we shall denote θ, and the extent of Co to C π-bonding can be established.

Such a relationship may be founded on the following argument. Let us suppose that to the extent that metal dπ electrons enter pπ orbitals of C, the C≡N pπ electrons are forced to occupy N pπ orbitals and that to this same extent these N pπ orbitals become hybridized with the s and pσ orbitals of N. Once an assumption is also made about the degree of s and p character in the orbital used by N in the σ part of the C≡N bonding, it is possible to formulate a set of three equivalent hybrid orbitals, one being used to bond the $-CH_3$ group, the other two holding unshared electrons.

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[32] C. C. Costain, *J. Chem. Phys.*, **29**, 872 (1958).

[33] Here and in the discussion immediately following, bond lengths mentioned without specific literature citations are from "Tables of Interatomic Distances and Configuration in Molecules and Ions," L. E. Sutton, Ed., The Chemical Society, London, 1958, pp. 512–519.

[34] While writing II and II′ in this convenient way, care should be taken to avoid a misapprehension regarding the directional properties of the electron distribution. Since, in general, the M–C π-bonding will take place through both of the carbon pπ orbitals which are perpendicular to the M–C axis, a shift of electrons from C to O or N will also take place in both of the corresponding O or N orbitals. Thus, M═C═O should not be taken to indicate trigonally hybridized O, with the lone pairs in two of the orbitals, but rather oxygen with its unshared electrons occupying a set of hybrid orbitals symmetrically distributed about the C–O axis. These may be written as linear combinations made up from p_x and p_y (taking the C–O line as the z axis) in equal amounts along with contributions from p_z and s.

(Thus they will not actually be equivalent, but we shall treat them as such for simplicity.) The mixing coefficients in these trigonally symmetric hybrids will be determined by the fractional contributions they can receive from N pπ orbitals. Once the correct algebraic expressions for them are written, the angles made by each of them with the C$\equiv$N axis can be computed; this angle can be identified with the C–N–C angle or its supplement, θ.

To illustrate, suppose we take the extreme case where the Co–C bond has a π-bond order of 2; that is, two electron pairs are back donated. Then both pπ orbitals on N are excluded from C$\equiv$N π-bonding and will be hybridized with the s and pσ orbitals of N. Now the remaining σ orbital used by N in the CN σ-bond may, in one extreme, be considered to retain sp character or, in the other extreme, be assumed to become a pure s orbital. In the latter case, the three orbitals to be hybridized will be the three p orbitals of N, and no hybridization need occur. The angle θ is easily shown to be 37.8°. However, if sp hybridization is retained in the N orbital used in CN bonding, the pσ character in the set of hybrid orbitals is reduced by one-half and the set of hybrid orbitals formed will make a larger angle, namely 55°. For smaller degrees of back donation, the contributions of the pπ orbitals of N to the hybrids will be proportionately smaller and the angle θ, on either assumption about the degree of s-pσ hybridization in the orbital used for CN σ bonding, will become smaller. The tangent of the angle θ will be proportional to the fraction of pπ orbitals used, and thus also proportional to the number of back-donated electrons, n. In this way the graph shown in Figure 3 can be constructed. The shaded area is bounded on the lower side by the curve for pure s character in the CN σ-bond and on the upper side by the curve for sp hybridization in the orbital used by N in the CN σ-bond. The proper result should lie between these limits, but there is no reliable way of fixing it more exactly.

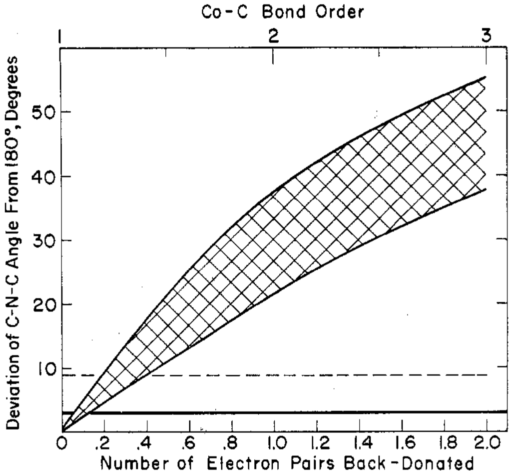

Figure 3.—Deviation of CNC angle from 180° plotted against Co–C bond order and number of electron pairs back donated from Co to C, according to the method of estimation explained in the text. The shaded area gives the range in angle between two extreme assumptions about hybridization. The solid horizontal line represents the observed angle of 3° while the dashed horizontal line represents the observed angle plus 4σ (σ = 1.5°), namely, 9°, which is taken as an extreme upper limit on the actual value of the angle.

We now examine Figure 3 to see whether the observed degree of bending is consistent with estimates which can be made for any given degree of Co to C π-bonding. If we assume the maximum error in θ, namely 4σ, so that $\theta = 9°$ (indicated by the horizontal dashed line) and we further assume that the C to N σ-bond is formed by a pure s orbital of nitrogen, even for small amounts of Co to C back bonding, the amount of such back bonding would correspond to a Co–C bond order of 1.4. This figure is below our estimates from the Co–C bond lengths even though it is obtained by making two very unlikely assumptions in order to maximize it. If we assume that θ is not greater than 7.5° (3° + 3σ) and that the carbon atom uses approximately sp hybridization, the degree of Co–C back bonding corresponds to a bond order of only 1.17, which seems far too low to explain the shortness of the Co–C bonds.

From these considerations, we draw the conclusion that the valence bond treatment of metal–isonitrile back bonding is not satisfactory, whereas a molecular orbital description is consistent with the structural data. It may be noted that the molecular orbital description has recently been used as the basis for a quantitative treatment of the bonding in Cr(CO)$_6$ with reasonable success.[35]

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(35) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).