terpretation of the moment it was assumed that since the molecules were "bulky" they would pack in such a way as to make *inter*molecular H–H interactions negligible. The authors thus assigned the total moment to the one *intra*molecular interaction and derived an H–H distance of 1.88 Å., which led them to the widely-quoted Fe–H distance of about 1.1 Å. (a hydrogen "buried" in the metal orbitals). The possibility of an important H–H interaction in $HMn(CO)_5$ makes unjustifiable the assumption that such an interaction does not occur in $H_2Fe(CO)_4$; in fact, if there is one such interaction (~2.4 Å. in length), then the derived Fe–H distance would be a normal one for a covalent bond (about 1.5 Å.).

Although the evidence from this and other studies,[9,10] and from the recent calculations of Lipscomb and his co-workers,[22,23] is strongly in favor of a metal–hydrogen bond of normal length and of a hydrogen atom that occupies a definite position in the coordination polyhedron of a parent or substituted transition metal carbonyl hydride, it still seems worthwhile to settle this question beyond any doubt, and for this reason a neutron diffraction study of $HMn(CO)_5$ is now in progress.

Acknowledgment.—We are indebted to W. N. Lipscomb for the samples of $HMn(CO)_5$. We are indebted to K. Shimaoka for his help in the design of the low-temperature apparatus.

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The Structure of the Deca(methylisonitrile)dicobalt(II) Cation; an Isostere of Dimanganese Decacarbonyl[1]

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A single crystal X-ray structure determination has been carried out on the red diamagnetic compound of empirical formula $Co(CNCH_3)_5(ClO_4)_2$, prepared by Sacco and Freni. Since $[Co(CNCH_3)_5]^{2+}$ is isoelectronic with $Mn(CO)_5$, a dimeric structure analogous to that in $Mn_2(CO)_{10}$ seemed likely and such a structure has been found. The Co–Co bond is 2.74 ± 0.01 Å. in length, the Co–C bonds are 1.82–1.92 Å. in length, and the idealized point group symmetry of the dinuclear cation is D_{4d}. Because of the relatively high standard deviations in the coordinates of light atoms, which are at least partially caused by librational motions of the perchlorate ions, the bond angles and bond lengths within the $CoCNCH_3$ moieties have not been obtained with sufficient accuracy to provide fully conclusive evidence regarding the nature and extent of Co–C $d\pi$–$p\pi$ bonding, but the rather short bond lengths do suggest that such bonding occurs to a significant extent.

Introduction

Some years ago Sacco and Freni[3] reported that the compound $Co(CNCH_3)_5(ClO_4)_2$ could be obtained in two forms, one light blue and paramagnetic (one unpaired electron per cobalt atom) and the other red and diamagnetic. The latter is the stable one in the solid state, but solutions of either form appeared to be the same, namely, blue and paramagnetic. Since $[Co(CNCH_3)_5]^{2+}$ is isoelectronic and nearly isosteric with $Mn(CO)_5$, it seemed to us plausible that the red form of the compound might contain dinuclear cations, $[(CH_3NC)_5CoCo(CNCH_3)_5]^{4+}$, isostructural[4] with $Mn_2(CO)_{10}$, but more easily dissociated, giving blue, paramagnetic $[Co(CNCH_3)_5]^{2+}$ ions. In order to test this hypothesis, it seemed necessary to verify the presence of the binuclear cations in the red crystals and to show that they do in fact contain a Co–Co bond. Only by a single crystal X-ray structural study could this be done. Such a study was therefore carried out and is described here.

Experimental

A supply of the compound was made available to us by Professor Sacco. This consisted mainly of aggregates and dendritic growths, but, with patience, useful single crystals were eventually located. These red-brown crystals were found to belong to the orthorhombic system, with cell dimensions $a = 13.17 \pm 0.02$, $b = 12.47 \pm 0.02$, and $c = 12.49 \pm 0.02$ Å. The approximate density, determined by flotation, was 1.5 g. cm.$^{-3}$. Taking 463 for the molecular weight of $Co(CNCH_3)_5(ClO_4)_2$ and 4 as the number of these molecules per unit cell, the density calculated is 1.50 g. cm.$^{-3}$. The systematic absences $h00$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$, determined from precession photographs, unambiguously indicate space group $P2_12_12$ (No. 18).

Intensities were recorded photographically by the equi-inclination Weissenberg method using a small crystal of maximum dimension *ca.* 0.4 mm. and Mo $K\alpha$ radiation. Equi-inclination levels $0kl$ through $10kl$ were obtained by the multiple film technique and the intensities were estimated visually using a calibration wedge prepared from the same crystal. No corrections were made for absorption—the linear absorption coefficient, μ, being 12 cm.$^{-1}$. Approximately 1200 independent reflections were obtained on the levels indicated. These were corrected for Lorentz and polarization factors and, when necessary (*i.e.*, those reflec-

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[1] Supported by the Army Research Office.
[2] Fellow of the Alfred P. Sloan Foundation.
[3] A. Sacco and M. Freni, *Gazz. chim. ital.*, **89**, 1800 (1959).
[4] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

Table I
Final Atom Parameters and Their Standard Deviations

Atom	x	y	z	B, Å.^{2}	$\times 10^3$			
					$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Co	0.0991	0.3286	0.2371	2.25	0.32	0.25	0.25	0.09
C_1	0.128	−0.097	0.178	2.7	2	1	2	0.5
C_2	0.079	0.082	0.093	3.1	2	1	2	0.5
C_3	0.057	0.163	0.292	2.7	2	1	2	0.5
C_4	0.109	−0.017	0.380	2.6	2	1	1	0.4
C_5	0.239	0.076	0.243	3.9	3	2	2	0.6
C_6	0.157	−0.290	0.089	4.4	3	2	2	0.5
C_7	0.056	0.157	−0.107	6.6	4	3	3	1.0
C_8	−0.013	0.348	0.364	4.6	3	3	2	0.7
C_9	0.138	−0.072	0.585	5.2	3	2	2	0.8
C_{10}	0.414	0.148	0.285	10.4	6	4	4	1.5
N_1	0.144	−0.179	0.141	3.9	2	2	2	0.5
N_2	0.063	0.109	0.007	3.5	2	2	2	0.5
N_3	0.023	0.243	0.326	3.2	2	2	2	0.4
N_4	0.129	−0.042	0.470	3.6	2	2	2	0.5
N_5	0.321	0.101	0.263	5.6	3	2	2	0.7
Cl_1	0.2082	0.4081	0.1254	4.25	0.80	0.68	0.66	0.19
Cl_2	0.3337	0.7469	0.3991	5.06	0.86	0.75	0.72	0.2
O_1	0.309	0.371	0.141	13.4	3	3	3	0.8
O_2	0.147	0.319	0.093	17.1	6	4	4	1.8
O_3	0.172	0.468	0.213	8.4	3	2	2	0.8
O_4	0.219	0.476	0.031	10.4	4	3	3	1.0
O_5	0.427	0.687	0.396	8.1	3	2	2	0.8
O_6	0.346	0.859	0.410	13.9	5	4	4	1.6
O_7	0.282	0.724	0.305	16.7	6	5	5	2.0
O_8	0.277	0.714	0.490	12.1	4	3	3	1.2

tions on upper levels), for elongation, using the graphical method devised by Phillips.[5] The data were given equal weights in all computations.

A three-dimensional Patterson synthesis was first computed using the measured $|F|^2$ values. This calculation and all subsequent electron density summations were carried out using the Fourier program ERFR-2.[6] From the position of the heaviest twofold rotation peak $2x$, $2y$, 0, it was immediately evident that the cation contained a cobalt–cobalt bond, the metal–metal bond distance being *ca.* 2.7 Å. The positions of the two other most prominent Harker peaks, $^1/_2$, $^1/_2 + 2y$, $2z$ and $^1/_2 + 2x$, $^1/_2$, $2z$, were also in accord with this choice of cobalt x and y coordinates. Positions were also derived for the two crystallographically independent chlorine atoms from a consideration of the possible cobalt to chlorine vectors. Inspection of a three-dimensional Fourier synthesis phased on the cobalt atom alone confirmed one of the chosen positions, but suggested an alternative position for the second chlorine atom, which was consistent with the Patterson synthesis. These three atoms were then used to phase a second electron density map. Analysis of this Fourier map yielded positions for the eight perchlorate oxygen atoms, although the coordinates obtained for these atoms were not very precise because the peaks were extremely diffuse and badly resolved. In the case of one of the anions there were also several extra peaks present, although these gave unlikely Cl–O distances and were thus taken to be spurious. Further Fourier syntheses, now using the oxygen atom coordinates for phasing as well, gave positions for eleven of the fifteen independent carbon and nitrogen atoms constituting the cation and established the close similarity of the structure to that of $Mn_2(CO)_{10}$. Refinement of the positional parameters and scale factors was commenced, using the diagonal term approximation least-squares program, ERBR-1.[7] After two cycles the individual isotropic thermal parameters were also permitted to vary and, as expected, those for some of the oxygen atoms increased to very large values. At this stage, further electron density summations gave the positions of the four remaining carbon atoms and these were then included in the diagonal least-squares refinement. Refinement in this manner decreased the residual to 0.22. A difference Fourier synthesis was now calculated in an effort to locate the oxygen atoms more precisely, and this suggested appreciable changes in the positions of the oxygen atoms of one of the anions; no other appreciable changes were indicated.

At this point, refinement was continued using a full-matrix least-squares program, SFLSQ-3,[8] and here, in addition to positional and thermal parameters, a different scale factor was included for each individual equi-inclination level (eleven in all, the relative values of which did not vary by more than 5% on refinement). After two cycles of refinement in this manner, the individual isotropic temperature factors for the oxygen atoms had increased to values ranging from 8 to 17, suggesting that the perchlorate ions were undergoing some form of libration or hindered rotation. The values of the thermal parameters for the apical isonitrile group of the cation also increased to much higher values (especially the methyl carbon) than those of the equatorial groups. Another difference Fourier was calculated at this point and, as expected, anomalies characteristic of anisotropic thermal motion in the oxygen atoms were very clear. More important, however, was the absence of any extra peaks around the chlorine atoms which would have been indicative of statistical disordering of the anions. The residual at this point stood at 0.16 and all predicted changes in positional and thermal parameters were less than their estimated errors.

It was decided to try to improve the individual structure factor agreement by assigning anisotropic thermal parameters to the chlorine and oxygen. Two cycles of refinement were carried out, allowing all positional parameters and the anisotropic thermal parameters of the anions to vary. The isotropic thermal parameters of the cation were kept fixed. The predicted shifts in the positional parameters of the majority of the light atoms were appreciable after the first cycle of anisotropic refinement, but convergence was reached after the second cycle. There were still some appreciable changes in the oxygen thermal parameters, but

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

(6) 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."

(7) J. H. Van den Hende, "Crystallographic Structure Factor and Least Squares Refinement Program for the IBM 7090," 1961.

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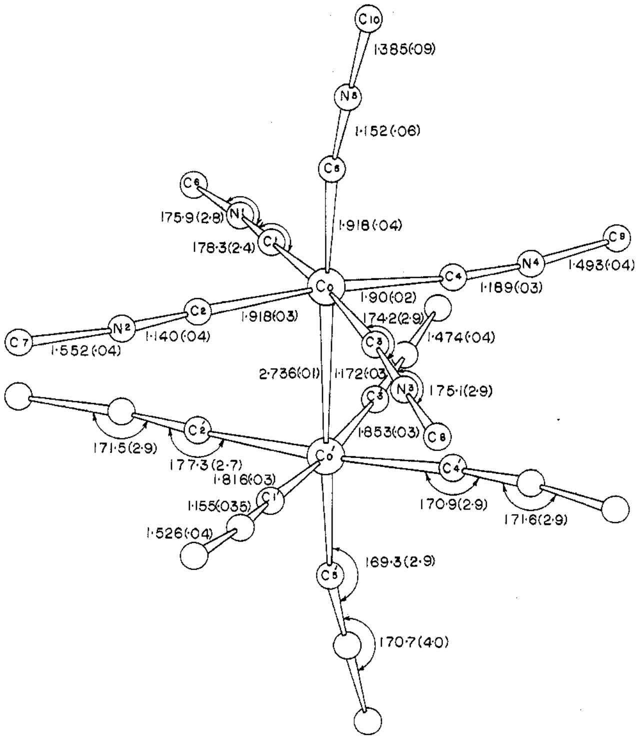

Fig. 1.—A perspective drawing of the $[Co_2(CNCH_3)_{10}]^{4+}$ ion, giving all crystallographically nonequivalent bond distances and all interbond angles, except C–Co–C angles, for which see Table III.

it is unlikely that much reliability can be attached to these values. Qualitatively, they do correspond to the anomalies on the difference map, although it is to be noted from Table II that the value for O_2 is physically impossible—the temperature factor not being positive definite. The final residual[9] stands at 0.13.

The final atomic positional parameters and isotropic thermal parameters are listed in Table I, together with their standard deviations. The isotropic thermal parameters are those obtained before the anisotropic refinement was commenced. The standard deviations are obtained from the usual least-squares formula $\sigma^2(j) = a_{ii}(\Sigma w\Delta^2)(m - n)$, where a_{ii} is the appropriate element of the matrix inverse to the normal equation matrix. The anisotropic thermal parameters, β_{ij}, for the chlorine and oxygen atoms are listed in Table II and they represent the ijth coefficients in the expression $\exp -(\beta_{11}h^2 + 2\beta_{12}hk + \beta_{22}k^2 + 2\beta_{13}hl + \beta_{33}l^2 + 2\beta_{23}kl)$. The atomic scattering factors used in this analysis were: for cobalt(II) that tabulated by Freeman and Watson[10]; for chlorine that tabulated by Dawson[11]; for carbon, nitrogen, and oxygen those tabulated by Hoerni and Ibers.[12] A table of the observed and final calculated structure factors has been deposited with the American Documentation Institute.[13]

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR THE PERCHLORATE IONS

	× 10^4					
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl_1	84	88	30.4	3	10.9	4
Cl_2	40	76	100	6.4	17.2	1
O_1	312	395	169	18	53	132
O_2	212	135	531	31	−100	−191[a]
O_3	157	141	106	51	22	43
O_4	210	78	265	78	48	77
O_5	31	97	243	47	−7	36
O_6	117	98	436	2	21	18
O_7	246	636	166	−125	−176	305
O_8	221	180	276	189	65	4

[a] Physically impossible.

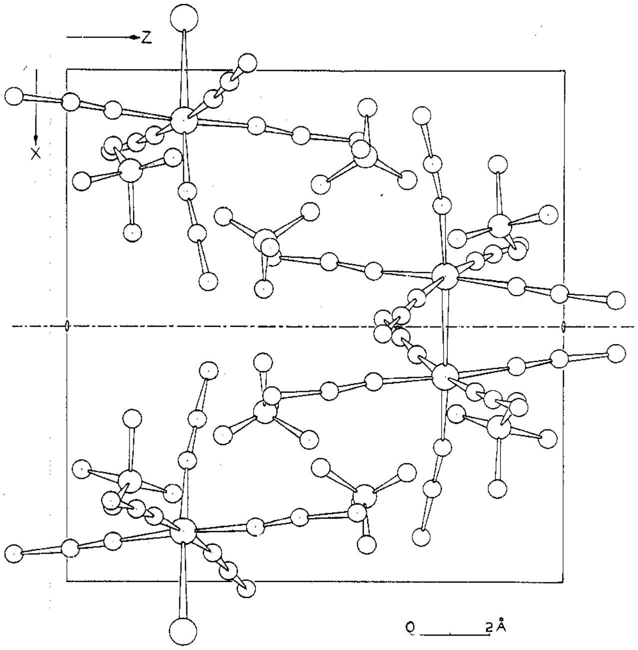

Fig. 2—A projection of the contents of one unit cell on the (010) face showing the packing, molecular orientations, and the location of the twofold symmetry axis, which bisects the Co–Co bond.

Discussion

The Dinuclear Cation.—The anticipated $[(CH_3NC)_5Co-Co(CNCH_3)_5]^{4+}$ ion does occur in red, diamagnetic $Co(CNCH_3)_5(ClO_4)_2$. Its structure is shown in Fig. 1, which also gives the interatomic distances and some of the interbond angles computed from the positional parameters of Table I. Although crystallographically the symmetry of the dinuclear cation is only C_2 (the twofold axis is shown in Fig. 2), the structure comes close to having D_{4d} symmetry. Each $-Co-(C)_5$ moiety approximates closely to an octahedral grouping with one vacant position and these two are jointed together through the Co–Co bond, so that the rotational configuration is the staggered one. Thus, as shown in Table IV, the several dihedral angles which should be 45° for the ideal staggered structure have values of 43, 43, 44, and 51°, each with a standard deviation of 2°. The twelve crystallographically independent bond angles about the cobalt atoms are listed in Table III; it may be seen that they are all within ±4° of 90°. Table IV gives the deviations of various atoms from certain mean planes of types which would contain all the listed atoms if each half of the molecule were precisely a fragment of an octahedron. It is clear that the devia-

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[9] Here and elsewhere in this paper, the residual is defined as
$$(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$$

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

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

[12] J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

[13] A table of observed and calculated structure factors has been deposited as Document No. 8081 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting in advance $3.75 for photoprints or $2.00 for 35-mm microfilm, payable to Chief, Photoduplication Service, Library of Congress

TABLE III

BOND ANGLES AROUND THE COBALT ATOM

$Co'–Co–C_1 = 86.1 \pm 0.8°$
$Co'–Co–C_2 = 87.9 \pm 1.0°$
$Co'–Co–C_3 = 88.9 \pm 0.9°$
$Co'–Co–C_4 = 88.3 \pm 0.9°$
$C_1–Co–C_5 = 93.9 \pm 1.3°$
$C_2–Co–C_5 = 94.4 \pm 1.3°$
$C_3–Co–C_5 = 91.3 \pm 1.3°$
$C_4–Co–C_5 = 89.5 \pm 1.1°$
$C_1–Co–C_2 = 85.7 \pm 1.2°$
$C_2–Co–C_3 = 91.8 \pm 1.3°$
$C_3–Co–C_4 = 87.5 \pm 1.0°$
$C_4–Co–C_1 = 94.7 \pm 1.3°$

TABLE IV

EQUATIONS OF MOLECULAR PLANES, DISTANCES OF ATOMS (IN Å.) FROM THESE PLANES, AND DIHEDRAL ANGLES

(1) Plane through Co, C_1, C_2, C_3, and C_4

$$0.9597X - 0.0109Y + 0.2808Z = 1.303$$

Co	0.03	N_1	−0.13	C_6	−0.34
C_1	−0.05	N_2	−0.12	C_7	−0.03
C_2	−0.03	N_3	−0.21	C_8	−0.30
C_3	−0.04	N_4	0.12	C_9	0.11
C_4	−0.03				

(2) Plane through Co, Co′, C_1, C_3, and C_5

$$-0.1168X - 0.9202Y + 0.3737Z = -2.725$$

Co	0.00	C_1	0.04	C_5	−0.08
Co′	0.00	C_3	0.04		

(3) Plane through Co, Co′, C_2, C_4, and C_5

$$-0.2827X + 0.3367Y + 0.8982Z = 0.998$$

Co	−0.00	C_2	0.01	C_5	−0.01
Co′	0.00	C_4	0.01		

Angles between Planes

(Co, Co′, C_1, C_3, C_5) and (Co, Co′, C_1', C_3', C_5') = 44 ± 2°
(Co, Co′, C_2, C_4, C_5) and (Co, Co′, C_2', C_4', C_5') = 51 ± 2°
(Co, Co′, C_1, C_3, C_5) and (Co, Co′, C_2', C_4', C_5') = 43 ± 2°
(Co, Co′, C_2, C_4, C_5) and (Co, Co′, C_1', C_3', C_5') = 43 ± 2°

tions of all the carbon atoms bound to cobalt atoms are below the level of significance.

The next feature of interest is the metal-to-metal distance, 2.736 ± 0.01 Å. This is appreciably shorter than that[4] in $Mn_2(CO)_{10}$, where it is 2.93 Å. We believe that the main reason for this is the inherently smaller size of a Co^{2+} ion relative to a manganese atom. While it is difficult to justify this quantitatively, it seems entirely reasonable from a qualitative point of view that the increased nuclear charge and, presumably, somewhat greater degree of effective ionization of metal atoms in $[Co_2(CNCH_3)_{10}]^{4+}$ compared to the isoelectronic Mn^0 would cause the former to be smaller by something on the order of 0.10 Å.

The existence of the bioctahedral configuration, without bridges, in this compound adds further weight to the belief that it is the preferred one for molecules isoelectronic with $Mn_2(CO)_{10}$. Indirect evidence, mainly from infrared spectra, has been adduced to show the existence of the same or very similar structures in $IFe(CO)_4–Fe(CO)_4I$,[14] several $Mn_2(CO)_8(PR_3)_2$ molecules,[15] in the dinuclear carbonylate anions, $[M_2(CO)_{10}]^{2-}$, of the group VI metals,[16] and in the $[Mn_2(CO)_8X_2]^{2-}$ anions.[17]

The Co–C–N–C Groups.—The dimensions and shapes of the five crystallographically independent Co–C–N–C groups may next be considered. The average values of various dimensions, with average standard deviations, are as follows: Co–C–N angle, 174 ± 3°; C–N–C angle, 172 ± 3°; $H_3C—N$ distance, 1.50 ± 0.05 Å.; C≡N distance, 1.15 ± 0.04 Å.; Co—C distance, 1.88 ± 0.04 Å. For comparison, the dimensions of the free CH_3NC molecule, from microwave spectroscopy,[18] are: C–N–C angle, 180.0° (by symmetry); $H_3C—N$ distance, 1.424 Å.; C≡N distance, 1.166 Å.

Because of the relatively large uncertainties in the distances and angles found in this study, stemming from the difficulties with the oxygen atom coordinates and from the large thermal motions of some of the methyl carbon atoms, only a limited amount of information can be derived concerning the nature of the bonding in the Co–C–N–C groups. Since we expect shortly to complete refinement of the structure of $[Co(CNCH_3)_5]ClO_4$, where metal–carbon back-bonding should be more extensive and the accuracy of the molecular dimensions higher, the present discussion will be brief.

The commonly recognized formulation for the back-bonding in metal–isonitrile complexes is that first proposed by Pauling[19] and represented by the following canonical forms.

$M—C\equiv\overset{+}{N}—CH_3$ $M=C=\ddot{N}—CH_3$

(linear) (bent)

According to this picture, for a resonance hybrid of these two canonical forms, one should find the following structural features: (1) the M–C bond will be shorter than an M–C single bond, (2) the C–N bond will be longer than in $CNCH_3$ itself, (3) the $N–CH_3$ bond may perhaps be somewhat lengthened due to a change in the hybridization of the nitrogen σ orbitals from sp to sp^2, (4) the C–N–C angle should be <180°, while (5) the M–C–N groups should remain linear. The agreement of our results with these expectations is fairly, but not entirely, satisfactory.

The mean Co–C distance, 1.88 Å., definitely seems to be shorter than the value which might be expected for a single bond, though the latter is difficult to estimate with certainty. Co^{II}–O distances of 2.05 Å. (in $Co(C_5H_7O_2)_2 \cdot 2H_2O$)[20] and 2.12 Å. (in $CoCl_2 \cdot 6H_2O$)[21] and Co–N(pyridine) of about 2.13 Å.[22,23] have been reported. Making an allowance of ∼0.05 Å. for the change in hybridization (sp^3 or sp^2 to sp) and correcting

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[14] F. A. Cotton, T. G. Dunne, B. F. G. Johnson, and J. S. Wood, *Proc. Chem. Soc.*, 175 (1964).

[15] A. G. Osborn and M. H. B. Stiddard, *J. Chem. Soc.*, 634 (1964).

[16] W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1964).

[17] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 434 (1964).

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

[19] *Cf.* L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 338.

[20] G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

[21] J. Mizuno, *J. Phys. Soc. Japan*, **15**, 1412 (1960).

[22] M. A. Porai-Koshits and G. N. Tischchenko, *Krystallografiya*, **4**, 239 (1959).

[23] J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

for differences in covalent radii (N < C by 0.07; O < C by 0.11), one might expect a Co^{II}–C(sp hybridized) bond to be about 2.15 ± 0.05 Å. Our results concerning metal–carbon bond lengths are thus in good accord with the view that there is appreciable metal–carbon double bonding. In this respect they are similar to the results obtained in the only previously published studies of isonitrile complexes, namely, those of Powell and co-workers on $Fe(CNCH_3)_6Cl_2 \cdot 3H_2O$[24] and $Fe(CNCH_3)_4(CN)_2$.[25] In these earlier studies, however, the results, ~1.85 Å. in the former compound and ~1.8 Å. in the latter, were subject to rather large and not accurately definable uncertainties.

The mean C≡N bond length, 1.15 ± 0.04 Å. in $[Co_2(CNCH_3)_{10}]^{4+}$, does not differ significantly from that in $CNCH_3$ itself, 1.17 Å. The relative insensitivity of bond length to bond order when the latter is ~3 means that no very great lengthening would have been expected, so that, considering also the standard deviation of 0.04 Å., the results do not disagree with expectation (2) above. It may be noted that in metal carbonyls, where extensive metal–carbon multiple bonding occurs and CO bond orders are often lowered considerably,[26] the C–O bond lengths are only some 0.02–0.03 Å. greater than that in CO itself.

The mean N–CH_3 bond length, 1.50 ± 0.05 Å., is considerably greater than that, 1.12 Å., in $CNCH_3$ itself. The apparent increase is more than would have been expected, but the large uncertainty leaves this point somewhat vague.

A decrease in the C–N–C angles from 180° to a mean value of 172 ± 3° is in good accord with expectation (4) and also in good agreement with results on the iron isonitrile compounds, where C–N–C angles of 173 and 167° were reported.[24,25]

The deviation of the Co–C–N angles from the expected value of 180° to 174 ± 3° is somewhat surprising. Within the limited accuracy of their results, Powell and co-workers considered the Fe–C–N angles to be 180°, but deviations of a few degrees would probably be possible. We have no simple explanation to offer for this result, other than to note that the standard deviation is large enough that the difference from 180° may not be significant.

The Perchlorate Ions.—As noted earlier, there were definite indications in the Fourier syntheses that the perchlorate ions are either disordered or, more likely, undergoing librational motion of large amplitude at room temperature. It is not unusual for this quasi-spherical ion to exhibit one or the other of these types of anomalous behavior. In $AgClO_4 \cdot 3C_4H_8O_2$, rotation was found to be so little hindered that the best fit to the diffraction data was obtained by treating the perchlorate ion as a chlorine atom concentrically enclosed by a spherical layer of electron density,[27] while disordering of the perchlorate ion has been observed in $[(CH_3)_3SO^+]ClO_4$.[28]

TABLE V

BOND DISTANCES AND ANGLES IN THE PERCHLORATE IONS

Distances, Å.		Angles, deg.	
Cl_1–O_1	1.42 ± 0.04	O_1–Cl_1–O_2	108.7 ± 2.6
Cl_1–O_2	1.43 ± 0.06	O_1–Cl_1–O_3	112.0 ± 1.9
Cl_1–O_3	1.40 ± 0.03	O_1–Cl_1–O_4	101.7 ± 2.2
Cl_1–O_4	1.46 ± 0.04	O_2–Cl_1–O_3	116.1 ± 3.4
Av. Cl–O	1.43 ± 0.04	O_2–Cl_1–O_4	106.2 ± 3.5
		O_3–Cl_1–O_4	110.6 ± 2.6
		Av. O–Cl–O	109.2 ± 3.0
Cl_2–O_5	1.44 ± 0.04	O_5–Cl_2–O_6	114.5 ± 2.4
Cl_2–O_6	1.41 ± 0.05	O_5–Cl_2–O_7	107.1 ± 3.2
Cl_2–O_7	1.39 ± 0.07	O_5–Cl_2–O_8	109.1 ± 2.2
Cl_2–O_8	1.42 ± 0.05	O_6–Cl_2–O_7	109.8 ± 4.1
Av. Cl–O	1.43 ± 0.05	O_6–Cl_2–O_8	105.4 ± 2.7
		O_7–Cl_2–O_8	110.9 ± 3.4
		Av. O–Cl–O	109.5 ± 3.5

The components of the anisotropic temperature factor tensors for the atoms of the perchlorate ions are given in Table II. Those for the oxygen atoms are mostly rather high. The 3 × 3 determinant of the six anisotropic thermal parameters of atom O_2 is nonpositive definite and thus physically inconsistent. However, we believe that the proposed solution, with ordered perchlorate ions having high amplitude librational motions or highly hindered rotational motions, is the most reasonable one. Other possibilities, namely, essentially free rotation, treated as described by Prosen and Trueblood,[27] and several sorts of disordering were tested but these did not lead to satisfactory behavior of the residual on least-squares refinement nor to acceptable dimensions for the perchlorate ions.

The bond distances and angles in the perchlorate ions which are obtained from the final atom positional parameters are listed in Table V. The average of the twelve O–Cl–O angles is 109.4° with a standard deviation of the mean of ~3°; thus none of the angles is significantly different from the expected tetrahedral angle. Similarly, the average Cl–O distance, 1.43 ± 0.05 Å., is in satisfactory agreement with the accepted value[27–29] for this parameter, 1.44 Å., in the absence of any correction due to the "shortening" effect of the libration.

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[29] Reference 19, Table 9-2, p. 321.