tion elements occupy the centers of the tetrahedra. As the B component becomes more and more metallic, the inverted stoichiometry A_4B_3 seems to be preferred and the atoms of the B component take over the central positions.

The occurrence of this structure with B component atoms having atomic radii ranging from 1.27 (S) to 1.66 (Sb) Å indicates that the sizes of these atoms do not influence the choice or the stability of the structure. However, the variations in the positional parameter x, represented in Table II, can be interpreted in terms of the variations in size. In the case of the A_3B_4 phases it appears that the parameter is not affected by the size of the B component atoms. (Compare the values for La_2Te_3 and La_3Se_4.) However, in the A_4B_3 phases it decreases with a decrease in the size of the B component atoms. (Compare the values for La_4Ge_3 and $La_4Rh_{\sim 3}$.)

$La_4Rh_{\sim 3}$ is the first representative of the Th_3P_4-type structure wherein both the component atoms are of transition elements. This structure has not yet been found in other rare earth–rhodium alloys.

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The Crystal and Molecular Structure of Tris(tetra-*n*-butylammonium) Octacyanomolybdate(V)

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The crystal and molecular structure of the tetra-*n*-butylammonium salt of the paramagnetic complex $Mo(CN)_8^{3-}$ has been determined by single-crystal X-ray diffraction methods and its electron spin resonance has been reexamined in light of the structural results. Intensity data were collected by counter techniques and the structure has been refined by least-squares methods to a conventional R factor of 0.094 for 597 nonzero independent reflections. The complex crystallizes in space group P4/ncc of the tetragonal system in a cell of dimensions $a = 17.009$ (5) Å, $c = 22.784$ (21) Å, and $V = 6592$ Å^3. An experimental density of 1.03 (4) g/cm^3 agrees with a calculated value of 1.03 g/cm^3 for $Z = 4$. The $Mo(CN)_8^{3-}$ anion possesses a slightly distorted triangular dodecahedral coordination geometry and is crystallographically required to have D_2 molecular symmetry. The two independent Mo–C bond distances do not differ significantly and have an average value of 2.12 (2) Å. Other important anion distances are the average C–N and Mo–N distances of 1.16 (2) and 3.27 (2) Å, respectively. The tetra-*n*-butylammonium cations exhibit significant disorder in the γ- and δ-carbon atoms of the butyl chains. The electron spin resonance spectrum of a polycrystalline sample of $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ has an isotropic g value of 1.991 ± 0.002 which agrees exactly with other values of $\langle g \rangle$ obtained from solution spectra or calculated from frozen-glass spectra. It is concluded that the $Mo(CN)_8^{3-}$ anion probably has the distorted dodecahedral coordination of D_2 symmetry in the solution state as well as in the crystalline state and that the unpaired electron occupies a metal-based orbital which has both $d_{x^2-y^2}$ and d_{z^2} character.

Introduction

There has been much discussion in the literature during the past decade concerning the geometry of discrete eight-coordination in transition metal complexes.[1-4] Particular attention in this area has been focused on the two octacyanomolybdate anions $Mo^{IV}(CN)_8^{4-}$ and $Mo^{V}(CN)_8^{3-}$. Recently, the crystal and molecular structure of $K_4[Mo(CN)_8]\cdot 2H_2O$, which was first reported 1939,[5] has been reinvestigated.[4] The triangular dodecahedral coordination of $Mo(CN)_8^{4-}$ has been confirmed, along with more accurate structural parameters, and an exhaustive exploration of the factors contributing to its dodecahedral geometry of approximate D_{2d} symmetry has been presented. The two d electrons of this anionic Mo(IV) complex occupy the d_{xy} orbital or, by the alternative symmetry definition, the $d_{x^2-y^2}$ orbital of the metal which can be used for limited π bonding with the ligands. In their discussion, Hoard, *et al.*,[4] stated that one of the two d electrons can be removed to give the paramagnetic complex $Mo^{V}(CN)_8^{3-}$ "with retention of the principal structural features"—that is, that the $Mo(CN)_8^{3-}$ anion should be dodecahedral. Electron spin resonance studies, however, have indicated that, at least in solution, the Mo(V) species exists as a square antiprism of D_{4d} symmetry.[6,7] Other physical data at this time appear to be inconclusive. Published Raman and infrared studies[8] of the $Mo(CN)_8^{4-}$ anion support the contention of D_{4d} symmetry in the solution state but are unable to eliminate the possibility of dodecahedral

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(1) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **51**, 109 (1967), and references therein.

(2) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967), and references therein.

(3) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(4) J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Am. Chem. Soc.*, **90**, 3177 (1968). Professor Hoard has pointed out to us that the phrase "with retention of the principal structural features" was intended to mean "only that the chemical and stereochemical integrity of the atomic grouping as a discrete eight-coordination complex" should be maintained in going from $Mo(CN)_8^{4-}$ to $Mo(CN)_8^{3-}$.

(5) J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).

(6) B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966).

(7) R. G. Hayes, *J. Chem. Phys.*, **44**, 2210 (1966).

(8) S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, **21**, 1087 (1965).

coordination known to exist for that complex in the crystalline state. On the other hand, a different, recently reported Raman study[9] of the $Mo(CN)_8{}^{4-}$ anion has shown that the complex *maintains* its dodecahedral geometry in going to the solution state and does not assume a square-antiprismatic configuration in solution. Results for the $Mo(CN)_8{}^{3-}$ anion in the same Raman study appear to be less conclusive.[9] In order to shed some light on the coordination geometry of the Mo(V) complex, we have determined the structure of $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ by single-crystal X-ray diffraction methods. The results of that determination together with a reexamination of the electron spin resonance of the Mo(V) species are presented in this paper.

Collection and Reduction of the X-Ray Data

The complex $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ was synthesized from $K_4Mo(CN)_8$ in the following manner. $K_4[Mo(CN)_8]$, which was prepared by the method of Furman and Miller,[10] was oxidized in an acidic solution by $KMnO_4$ and the Ag^+ salt of the $Mo(CN)_8{}^{3-}$ anion was precipitated out by the addition of $AgNO_3$. The brown, amorphous precipitate was washed and added to dilute HCl. The resulting AgCl was then filtered off and excess $[(n\text{-}C_4H_9)_4N]Br$ was added to the acidic solution containing $Mo(CN)_8{}^{3-}$. $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ precipitated from the solution as a light greenish yellow powder. Beautiful transparent yellow crystals suitable for single-crystal X-ray work were grown from acetonitrile–ether solutions. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$: C, 65.2; N, 14.9; H, 10.4; O, 0.0. Found: C, 65.4; N, 14.9; H, 10.5; O, <0.5. Elemental analyses were performed by Midwest Microlab, Inc.

It was quickly apparent that the crystals of $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ were sensitive to both light and X-rays. Although decomposition of the crystals in the X-ray beam was sufficiently slow to allow for the collection of intensity data from a single crystal, several crystals had to be used for preliminary measurements including the unit cell and space group determinations. The crystals were examined by optical goniometry and standard film methods. Precession photographs, taken with Mo Kα radiation (λ 0.7107 Å), revealed that the complex crystallizes in a tetragonal unit cell of refined dimensions a = 17.009 (5) Å, c = 22.784 (21) Å, and V = 6592 Å^3. An experimental density of 1.03 ± 0.04 g/cm^3 obtained by flotation in zinc chloride solutions agrees with a calculated value of 1.03 g/cm^3 for four molecules in the unit cell. The observed extinctions of $hk0$ for $h + k$ odd, $h0l$ for l odd, and hhl for l odd are consistent with the space group P4/ncc.[11] The precession photographs also revealed that the hkl reflections for which $h + k$ and l are both even are generally much stronger than those reflections for which either or both of the quantities $h + k$ and l are odd. Thus, the complex is required to possess some crystallographic symmetry and the molybdenum ion must occupy one of the fourfold special positions of the space group.

The intensity data were collected at room temperature from a single crystal using a Picker four-circle automated diffractometer. The θ–2θ scan technique was employed with a scan rate of 1°/min and 10-sec background counts collected at both ends of the 2θ scan range. Ni-filtered Cu Kα radiation was employed. Prior to the beginning of data collection, the crystal was aligned along the tetragonal axis by optical goniometry and with a number of precession photographs. The crystal was then placed on the diffractometer and approximately 15 reflections were carefully centered in the counter aperture. The unit cell parameters and orientation angles were refined by the least-squares procedure of W. C. Hamilton's MODEl diffractometer setting program.[12]

The intensities of two independent sets of reflections in one octant of reciprocal space were collected out to a maximum 2θ value of 90°. A total of 2601 intensities were measured. During the data collection, the intensity of the 336 reflection, which was monitored at least once every 150 reflections, showed a decrease of approximately 30% of its original value. In the processing of the data, the intensities of all reflections were corrected for decomposition based on the assumption that the decomposition was isotropic. The data were then corrected for background, and Lorentz–polarization factors were applied to the observed intensities to yield a set of $F_o{}^2$ values where F_o is the observed structure factor amplitude. The two independent data sets were then averaged for all subsequent calculations. No absorption correction was made in view of the relatively small linear absorption coefficient (μ = 20.3 cm^{-1}). The crystal used for the data collection was a rectangular parallelipiped showing development of the $\{110\}$ and $\{001\}$ faces and having approximate dimensions 0.40 × 0.30 × 0.15 mm with the longest direction corresponding to the c axis of the crystal.

Solution and Refinement of the Structure

The Mo ion was assigned to the 4(a) special positions of 222 site symmetry on the basis of a three-dimensional Patterson function and packing considerations. The two independent cation nitrogen atoms were then assigned to the 4(b) and 8(f) special positions of the space group. The positions of the anion cyanide groups and 11 of the 12 independent cation carbon atoms were determined from a number of difference Fourier maps based on phases obtained from the refined positions of the located atoms. In the preliminary cycles of least-squares refinement, each atom was assigned an individual isotropic thermal parameter

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[9] T. V. Long, Paper No. 57, The New York Regional Meeting of the American Chemical Society, New York, N. Y., May 1–2, 1969, and private communication.

[10] N. H. Furman and C. O. Miller, *Inorg. Syn.*, **3**, 160 (1950).

[11] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962, p 226. In the refinement, the second setting of P4/ncc with the origin at $\bar{1}$ was employed.

[12] In addition to the MODEl setting program, the main programs for the IBM 360/50 used in this work were local versions of the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the Busing–Martin–Levy ORFFE function and error program, and C. K. Johnson's ORTEP plotting program. Various other local programs were also used in the investigation.

Table I

Final Positional and Thermal Parameters for $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$

	x	y	z	B, Å^2
Mo	−0.250	0.250	0.250	[a]
C_1[b]	−0.142 (2)[c]	0.282 (1)	0.289 (1)	8.2 (8)
N_1	−0.084 (1)	0.304 (1)	0.310 (1)	10.6 (6)
C_2	−0.215 (1)	0.162 (1)	0.311 (1)	6.9 (7)
N_2	−0.199 (1)	0.116 (1)	0.346 (1)	10.3 (6)
BUN1	−0.250	0.250	0.000	13.4 (9)
BUN2	−0.009 (2)	0.009	0.250	12.9 (9)
BU1C1	−0.281 (2)	0.184 (2)	0.042 (1)	13 (1)
BU1C2	−0.323 (2)	0.110 (2)	0.009 (2)	18 (1)
BU1C3	−0.366 (4)	0.051 (5)	0.039 (3)	30 (3)
BU1C4	−0.371 (4)	−0.015 (5)	0.006 (3)	28 (3)
BU2C1	0.002 (2)	−0.073 (3)	0.288 (2)	11 (1)
BU2C2	−0.066 (3)	−0.066 (3)	0.339 (2)	15 (1)
BU2C3	−0.052 (3)	−0.150 (4)	0.391 (3)	22 (3)
BU2C4	−0.089 (3)	−0.186 (3)	0.335 (2)	21 (2)
BU2C5	−0.011 (2)	0.080 (3)	0.290 (2)	11 (1)
BU2C6	0.070 (2)	0.094 (3)	0.321 (2)	15 (1)
BU2C7	0.061 (2)	0.165 (3)	0.373 (2)	16 (1)

[a] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The anisotropic thermal parameters for Mo are $\beta_{11} = \beta_{22} = 0.00487$ (9), $\beta_{33} = 0.00319$ (7), $\beta_{12} = -0.0004$ (4), and $\beta_{13} = \beta_{23} = 0.0$. [b] C1–N1 and C2–N2 are the two independent cyanide groups. BUN1 is the cation nitrogen atom in the 4(b) special positions while BUN2 is the other independent cation nitrogen atom located in the 8(f) special positions of the space group. BU1C1 is attached to BUN1 and the other carbon atoms in the chain are numbered successively. BU2C1 and BU2C5 are both attached to BUN2 with the other atoms numbered accordingly. BU2C8 was not located because of disorder. [c] The numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures.

which was varied along with the positional parameters of the atom. It was noted that all of the cation thermal parameters were quite large, especially those assigned to the γ- and δ-carbon atoms of the *n*-butyl groups. All attempts at determining the position of the remaining carbon atom, corresponding to the terminal methyl group of one of the *n*-butyl chains, proved unsuccessful and we concluded that its position was completely disordered. The extremely low density of the crystal, a model of the packing, and all subsequent refinements and difference Fouriers lend support to the notion of significant disorder in the alkyl chains of the cations.

The trial structure was refined by a least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$ where the weights w were assigned in the following way: for $F_o < 35$, $w = (F_o/105)^2$; for $35 \leq F_o \leq 80$, $w = (^1/_3)^2$; and for $F_o > 80$, $w = [1.0/(3.0 + 0.15F_o/80)]^2$. The merits of this weighting scheme as opposed to one based on counting statistics are discussed below. The neutral Mo, C, and N scattering factors were obtained from Ibers' tabulation[13] while the anomalous parts of the Mo scattering factor were obtained from Templeton's tabulation[14] and were included in the calculated structure factors.[15] Only those reflections for which the observed F^2 value was greater than twice the value of $\sigma(F^2)$ were included in the final refinements and in the calculation of the discrepancy indices. The standard deviations $\sigma(F^2)$ were estimated according to the formula

$$\sigma(F^2) = \frac{1}{TLp}[C + (t_c/2t_b)^2(B_1 + B_2) + (0.03I)^2]^{1/2}$$

where C is the total integrated count obtained in a scan of time t_c, B_1 and B_2 are the two background counts, each obtained in time t_b, I is the net integrated count, Lp is the Lorentz–polarization factor, and T is the transmission coefficient.

In the initial round of calculations, all atoms were restricted to isotropic thermal models. This refinement of 65 parameters including one variable scale factor converged to an R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.115 and a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$) of 0.138. A difference Fourier based on this refinement provided evidence for anisotropic thermal motion of the molybdenum ion. After the elimination of a number of data errors which were due to either incorrect positioning or punching errors, a final refinement was carried out in which the Mo ion was described by an anisotropic thermal expression while all other atoms were restricted to the isotropic vibration model. This refinement of 67 positional, thermal, and scale parameters converged to a conventional R factor of 0.094 and a weighted R factor of 0.085 for 597 independent reflections above 2σ. A final difference Fourier showed no peaks higher than approximately 30% of the height of an average carbon atom in this structure.

The parameters obtained in this final round of calculations are taken as the final parameters of the structure and are given in Table I. Standard deviations, as obtained from the inverse matrix, are also given. In Table II, the values of F_o and $|F_c|$ (in electrons × 10) are given for the 597 reflections used in the refinement. With the weighting scheme employed, the values of $w^{1/2}(F_o - F_c)$ are found to exhibit a normal Gaussian distribution and the estimated standard deviation of an observation of unit weight is calculated to be 1.38. This value, which is indicative of the appropriateness of the weighting scheme, is considerably closer to 1.0 than the corresponding values obtained with different weighting schemes based on counting statistics. In addition, for each of several weighting schemes employed, it was found that the weak reflections consistently gave the poorest agreement. It appears that the intensities of the weak reflections, which are in general solely dependent on light-atom contributions, are most seriously affected by the observed decomposition and the disorder in the alkyl chains of the cations. Hence, the weak reflections are assigned excessive weights in a scheme based solely on counting statistics and are more correctly weighted in the scheme described above.

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(13) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, Table 3.3.1A.

(14) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, Table 3.3.2B.

(15) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10) FOR $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$

H	K	FOBS	FCAL
******L= 0******			
0	8	336	455
0	6	1168	1274
0	4	650	753
0	2	490	559
0	10	211	287
0	12	614	641
0	14	146	162
1	15	264	227
1	5	639	594
1	11	459	371
1	13	355	400
1	9	756	723
1	7	1179	1145
2	14	407	409
2	8	1065	1048
2	6	1341	1439
2	12	365	375
2	10	899	945
3	15	287	295
3	9	830	869
3	7	1106	1259
3	5	990	1026
3	11	927	924
3	1	137	261
4	12	609	692
4	14	330	362
4	6	1097	1056
4	10	931	962
4	8	1135	1194
4	4	212	206
5	13	413	479
5	7	669	756
5	9	897	909
5	11	675	605
5	5	956	923
6	12	465	494
6	14	335	354
6	10	574	547
6	6	399	398
6	8	600	619
7	13	341	343
7	11	488	473
7	7	444	405
7	9	590	598
8	12	354	329
8	10	492	497
8	8	508	522
9	11	390	402
9	9	447	421
10	10	428	413
11	11	201	214
13	3	495	444
******L= 1******			
1	4	164	291
1	12	140	105
1	9	157	96
1	5	396	417
1	6	230	183
1	7	214	210
1	10	87	131
2	7	157	73
2	8	126	47
2	5	97	259
2	6	598	433
2	3	186	51
3	7	364	466
3	5	392	514
3	4	428	406
4	7	134	98
4	6	291	247
4	9	104	82
4	5	225	287
6	7	89	142
10	11	127	79
******L= 2******			
0	3	335	350
0	4	1633	1730
0	5	647	611
0	6	1384	1316
0	7	204	283
0	8	715	708
0	9	119	156
0	10	363	382
0	14	154	159
0	12	629	625
0	1	159	306
1	15	227	209
1	4	298	259
1	11	569	528
1	13	345	359
1	9	941	911
1	2	160	116
1	5	856	900
1	7	903	888
1	8	202	209
2	6	913	868
2	8	920	926
2	10	931	910
2	14	339	360
2	4	170	159
2	12	397	384
2	9	153	158
3	3	177	110
3	13	410	396
3	9	776	756
3	11	678	773
3	15	259	274
3	5	807	743
3	7	1100	1035
3	6	92	14
4	12	601	593
4	14	290	310
4	4	704	903
4	6	907	954
4	10	730	730
4	8	846	862
4	5	97	61
5	13	366	420
5	5	675	644
5	7	689	723
5	9	133	182
5	11	597	530
6	9	771	770
6	10	565	516
6	12	383	392
6	14	308	315
6	5	549	603
7	13	315	304
7	7	594	656
7	11	393	375
7	9	603	582
8	12	310	302
8	9	565	529
8	10	453	443
9	9	419	401
9	11	324	336
10	13	339	338
******L= 3******			
1	4	225	199
1	9	244	217
1	2	324	313
1	3	1510	1374
1	5	1091	1155
1	6	129	128
1	8	133	174
1	10	102	90
2	8	339	185
2	10	120	162
2	6	650	605
2	4	1497	1407
2	3	203	255
2	9	127	72
3	5	141	78
3	7	577	440
3	6	213	209
3	4	116	237
4	7	143	114
4	6	138	97
4	10	114	77
4	5	399	447
5	3	91	70
5	6	323	338
5	7	95	127
6	7	99	138
8	12	111	96
******L= 4******			
4	3	637	664
0	5	421	447
0	7	115	104
0	9	101	1
0	12	569	594
0	14	235	280
0	10	470	514
0	4	2285	2199
0	3	102	4
0	2	1197	1180
0	1	165	205
0	0	2566	2574
1	1	2965	3038
1	11	682	691
1	15	274	254
1	13	345	397
1	9	803	757
1	2	167	36
1	3	847	852
1	4	107	184
1	5	1493	1522
1	6	387	426
1	7	801	830
1	8	97	19
2	7	324	246
2	8	574	653
2	10	849	816
2	14	334	352
2	6	1039	1053
2	4	977	1040
2	5	233	286
2	3	108	0
2	12	421	438
2	9	128	132
3	13	381	373
3	9	735	732
3	11	494	505
3	15	278	279
3	5	1021	1122
3	8	82	97
3	7	1055	1001
3	6	284	123
3	4	194	459
4	12	477	483
4	14	287	291
4	6	1054	1009
4	10	551	597
4	5	207	281
5	5	852	797
5	9	659	665
5	8	157	269
5	13	355	384
5	7	759	707
5	11	554	527
6	10	556	566
6	12	376	380
6	14	289	308
6	6	702	769
6	9	115	193
7	13	319	324
7	7	749	727
7	11	391	420
7	9	608	612
8	12	356	355
8	8	569	527
8	10	459	475
9	9	436	458
9	11	336	322
10	10	312	313
******L= 5******			
4	10	132	101
1	2	764	769
1	3	936	728
1	4	339	376
1	5	1256	1228
1	7	192	205
1	8	240	153
1	9	240	222
2	7	193	190
2	8	273	171
2	10	212	201
2	6	846	812
2	4	590	628
2	5	358	496
2	3	632	703
2	11	114	63
2	9	97	86
3	9	108	196
3	10	159	163
3	5	373	321
3	8	96	125
3	6	282	160
3	4	351	435
4	6	228	174
4	9	109	101
4	5	137	114
5	9	122	121
5	7	121	84
6	7	213	236
7	11	98	115
******L= 6******			
4	10	379	358
0	14	291	317
0	12	464	466
0	9	165	153
0	10	678	734
0	8	1331	1156
0	6	278	412
0	4	1893	1992
0	3	779	711
0	2	795	699
0	1	487	461
0	0	2221	2250
1	11	644	597
1	1	195	308
1	13	329	366
1	2	731	723
1	3	962	840
1	4	515	535
1	5	1512	1321
1	6	161	189
1	7	746	754
1	9	738	698
2	7	147	124
2	8	398	413
2	10	640	635
2	2	1275	1332
2	14	298	308
2	6	1031	968
2	4	1048	982
2	5	220	155
2	12	358	371
3	13	307	319
3	9	607	594
3	10	101	128
3	3	1933	2031
3	11	348	345
3	5	663	616
3	7	441	552
3	6	92	179
3	4	106	198
4	12	367	361
4	14	249	250
4	7	81	68
4	6	581	588
4	8	557	506
5	9	469	445
5	13	289	281
5	7	729	696
5	11	402	398
6	10	472	456
6	6	777	784
6	12	288	298
7	7	768	729
7	13	267	266
7	11	342	368
7	9	570	506
8	8	516	490
8	12	319	315
8	10	343	350
9	9	380	399
9	11	279	274
10	10	290	296
******L= 7******			
4	8	142	219
1	2	443	377
1	3	220	277
1	5	584	571
1	6	267	239
1	7	482	291
1	9	338	278
2	8	209	206
2	10	185	210
2	4	256	318
2	3	94	49
3	9	273	231
3	10	113	70
3	5	363	213
3	8	116	100
3	7	154	194
3	4	214	193
4	7	139	207
4	5	76	148
5	9	92	107
5	13	133	117
6	12	123	93
6	7	119	217
7	11	134	117
7	8	100	159
******L= 8******			
0	12	350	380
0	10	653	673
0	9	246	333
0	7	139	248
0	6	416	570
0	5	185	296
0	4	1300	1146
0	3	371	383
0	2	628	638
0	1	80	160
0	14	336	373
0	0	272	235
1	11	442	443
1	1	419	366
1	13	348	372
1	2	146	143
1	3	944	993
1	4	402	412
1	5	922	920
1	7	1187	999
1	8	247	218
1	9	743	687
1	10	97	84
2	2	806	802
2	7	180	114
2	8	634	618
2	10	521	499
2	14	302	309
2	6	1225	1153
2	4	977	1046
2	5	102	9
2	3	100	156
2	12	305	344
3	13	274	297
3	9	676	638
3	11	316	329
3	5	960	883
3	7	695	714
4	12	328	303
4	6	887	767
4	10	371	369
4	8	725	747
5	5	1181	1199
5	9	475	478
5	13	257	239
5	7	815	773
5	11	366	353
6	6	867	947
6	10	449	449
6	12	300	285
7	7	538	564
7	11	354	368
7	9	446	387
8	8	466	455
8	10	274	290
9	9	323	347
9	11	301	286
10	10	331	319
******L= 9******			
1	3	230	242
1	5	169	93
1	6	209	148
1	7	143	210
1	9	162	113
2	4	200	129
2	3	130	96
3	5	99	150
3	6	214	220
3	4	160	148
4	8	108	130
4	5	416	442
5	6	256	269
7	11	116	103
******L= 10******			
0	12	306	264
0	10	430	413
0	9	106	111
0	8	559	563
0	7	155	30
0	6	640	666
0	5	207	233
0	4	880	837
0	3	243	117
0	2	796	825
0	1	91	145
1	13	341	301
1	11	271	301
1	1	640	644
1	2	125	61
1	3	947	863
1	4	257	189
1	5	680	696
1	6	238	222
1	7	709	632
1	9	529	498
2	10	341	335
2	2	815	901
2	6	763	748
2	4	718	653
2	5	185	282
2	3	92	1
2	12	236	305
3	13	259	268
3	9	440	398
3	11	292	204
3	3	927	919
3	5	793	908
3	7	459	527
3	4	113	135
4	12	277	262
4	4	901	909
4	6	427	471
4	8	539	610
5	9	457	411
5	5	504	583
5	7	636	617
5	11	305	279
6	12	246	243
6	10	375	373
7	7	404	451
7	11	292	293
7	9	307	290
8	8	396	393
8	10	250	241
8	2	470	510
9	9	287	287
10	4	255	302
******L= 11******			
1	2	316	261
1	3	214	158
1	4	153	112
1	6	137	71
2	6	174	58
2	5	149	188
2	3	208	305
3	5	111	94
3	8	100	142
3	4	90	34
4	5	202	246
5	6	110	153
******L= 12******			
0	12	357	276
0	10	290	368
0	8	529	505
0	7	225	253
0	6	685	701
0	5	116	114
0	4	589	587
0	3	124	113
0	2	618	643
0	1	108	130
1	11	311	326
1	2	173	195
1	3	754	693
1	5	647	610
1	6	264	315
1	7	705	594
1	9	490	444
2	2	594	634
2	8	526	509
2	10	343	341
2	6	715	696
2	12	326	317
3	3	524	511
3	9	403	390
3	11	301	303
3	5	774	867
3	7	573	589
4	4	767	800
4	12	262	241
4	6	577	492
4	8	521	581
4	10	295	312
5	5	576	555
5	9	391	389
5	7	496	504
5	11	238	261
6	10	340	339
7	7	327	404
7	9	322	282
8	8	366	380
9	9	278	269
******L= 13******			
2	10	127	104
3	9	150	122
4	8	135	102
5	9	120	107
******L= 14******			
0	10	269	302
0	8	262	276
0	6	393	451
0	4	498	528
0	3	101	41
1	11	323	289
1	3	628	646
1	5	576	501
1	6	121	124
1	7	346	346
1	9	276	280
2	8	262	261
2	10	256	277
2	6	425	484
2	2	479	523
3	9	237	262
3	11	250	260
3	5	480	528
3	7	307	341
3	3	444	482
4	6	245	256
4	10	214	233
4	8	299	372
5	9	301	270
5	7	269	316
5	5	285	391
6	8	171	212
6	6	396	475
7	7	292	323
7	9	319	263
8	8	311	335
******L= 16******			
0	10	255	257
0	8	312	264
0	6	370	332
0	4	446	432
0	2	483	533
0	0	453	468
1	3	510	462
1	5	471	416
1	7	366	309
1	9	255	239
1	1	492	485
2	8	243	232
2	6	369	424
2	2	460	398
3	9	247	255
3	5	363	387
3	3	449	421
4	4	461	454
5	5	417	357
6	8	204	214
6	6	371	326
7	7	226	257
******L= 18******			
0	4	259	324
0	6	188	233
0	0	329	385
1	3	362	307
1	5	326	294
1	6	114	117
1	7	239	228
2	2	230	323
2	6	214	287
3	3	219	299
3	5	202	254
4	4	208	292
5	5	180	234
******L= 20******			
1	3	273	238

Description of the Structure

The most interesting and important feature of the structure is the coordination geometry of the $Mo(CN)_8^{3-}$ anion. This anion, which is crystallographically required to possess a minimum D_2 molecular symmetry, has an essentially dodecahedral coordination geometry according to the various criteria proposed by Hoard and Silverton[3] and by Lippard and Russ.[16] Important intramolecular distances and angles are summarized in Table III and a stereoscopic drawing of the anion is presented in Figure 1. The triangular dodecahedron which has an ideal symmetry of D_{2d} or $\bar{4}2m$ can be considered as consisting of two mutually perpendicular trapezoids whose line of intersection contains the metal ion and coincides with the $\bar{4}$ symmetry axis. In this geometry, there are two different ligand environments. However, we find that in the present structure, the two independent Mo–C distances do not differ significantly and average 2.12 (2) Å. The apparent equality of the two different metal–ligand distances in the dodecahedral geometry has also been observed by Hoard, *et al.*,[4] for the related complex $K_4[Mo(CN)_8]\cdot 2H_2O$ in which the Mo–C distances average 2.163 Å. Other important distances in the $Mo(CN)_8^{3-}$ anion are the average C–N distance of 1.16 (2) Å and the average Mo–N chain length value of 3.27 (2) Å.

TABLE III

PRINCIPAL INTRAMOLECULAR DISTANCES AND ANGLES

Distances	Value, Å	Angles	Value, deg
		Anion	
Mo–C1	2.11 (3)	Mo–C1–N1	176 (2)
Mo–C2	2.12 (3)	Mo–C2–N2	177 (2)
Mo–N1	3.27 (2)	C1–Mo–C1′	74 (1)
Mo–N2	3.28 (2)	C2–Mo–C2″	92 (1)
C1–N1	1.16 (3)	C2–Mo–C2‴	98 (1)
C2–N2	1.16 (3)	C1–Mo–C2	70 (1)
C1–C1′ (*a* edge)[a]	2.56 (5)	C1–Mo–C2″	75 (1)
C1–C2 (*m* edge)	2.44 (3)	C1–Mo–C2‴	77 (1)
C2–C2″ (*b* edge)	3.06 (5)		
C2–C2‴ (*b* edge)	3.20 (5)		
C1–C2″ (*g* edge)	2.58 (3)		
C1–C2‴ (*g* edge)	2.64 (4)		
		Cation	
BUN1-BU1C1	1.57 (3)	BU1C1–BUN1–BU1C1′	104 (2)
BU1C1-BU1C2	1.64 (4)	BU1C1–BUN1–BU1C1″	112 (1)
BU1C2-BU1C3	1.43 (6)	BU2C1–BUN2–BU2C5	112 (1)
BU1C3-BU1C4	1.35 (7)	BU2C1–BUN2–BU2C5′	115 (2)
BUN2-BU2C1	1.64 (4)	BU2C1–BUN2–BU2C1′	95 (3)
BU2C1-BU2C2	1.65 (4)	BU2C5–BUN2–BU2C5′	108 (4)
BU2C2-BU2C3	1.86 (6)	BUN1–BU1C1–BU1C2	114 (3)
BU2C3-BU2C4	1.55 (6)	BUN2–BU2C1–BU2C2	104 (3)
BUN2-BU2C5	1.51 (5)	BUN2–BU2C5–BU2C6	111 (3)
BU2C5-BU2C6	1.57 (5)	BU1C1–BU1C2–BU1C3	123 (5)
BU2C6-BU2C7	1.71 (5)	BU2C1–BU2C2–BU2C3	108 (4)
		BU2C5–BU2C6–BU2C7	110 (3)
		BU1C2–BU1C3–BU1C4	109 (7)
		BU2C2–BU2C3–BU2C4	74 (3)

[a] The primes denote symmetry-related atoms.

In their discussion of the stereochemistry of discrete eight-coordination, Hoard and Silverton defined a number of shape parameters which can be used to describe the coordination polyhedra in eight-coordinate structures.[3] The two angular-shape parameters θ_A and θ_B, which represent angles between the $\bar{4}$ axis of the dodecahedron and the two different metal–ligand bonds, are found to be 37.2 and 72.5°, respectively, in this structure. Other shape parameters for describing the dodecahedron are summarized in Table IV along with the corresponding values for $Mo(CN)_8^{4-}$ and the "most favorable" values for these parameters as determined by Hoard and Silverton.[3]

Lippard and Russ[16] have suggested the planarity of

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(16) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).

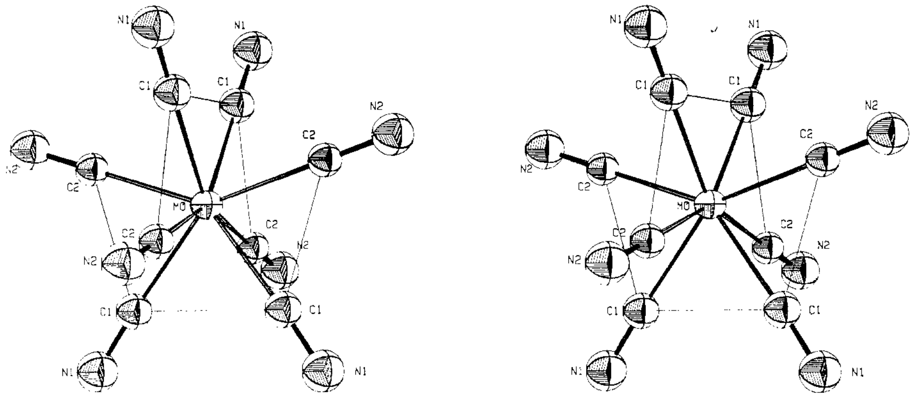

Figure 1.—A stereoscopic drawing of the $Mo(CN)_8^{3-}$ anion. The thermal ellipsoids are scaled to 15% probability distributions.

Table IV

Normalized "Shape" Parameters for the $Mo(CN)_8^{3-}$ Coordination Polyhedron and the "Most Favorable" Values Calculated by Hoard and Silverton[a]

Shape parameter	$Mo(CN)_8^{3-}$	$Mo(CN)_8^{4-}$ [b]	"Most favorable"[c]
a	1.21	1.18	1.17
g	1.22	1.24	1.24
	1.24		
m	1.15	1.16	1.17
b	1.45	1.47	1.50
	1.51	1.48	
θ_A, deg	37.2	36.0	35.2
θ_B, deg	72.5	72.9	73.5
M–A/M–B	1.00	1.00	1.03

[a] Definition of the shape parameters is given in ref 3 and the "most favorable" values are taken from Table I of ref 3. [b] Reference 4. [c] Intended primarily for d^0 MO_8 groups, most specifically ZrO_8.

the two trapezoids and the dihedral angle between them as the two least ambiguous criteria for assigning the eight-coordination polyhedron. The best least-squares planes through the atoms defining the two trapezoids are given by the equations

$$0.490x - 0.490y - 0.721z = -8.724$$

$$-0.490x + 0.490y - 0.721z = 0.058$$

in Cartesian coordinates. The deviations of the atoms C_1 and C_2 and the symmetry-related atoms C_2' and C_1' from the appropriate least-squares plane are 0.02, −0.01, 0.01, and −0.02 Å, respectively. On the basis of the χ^2 value for these four atoms, they can be considered to be rigorously planar. The dihedral angle between the two least-squares planes is found to be 87.7° as opposed to the ideal value of 90° for the dodecahedron and 77.4° for the square antiprism. It can be concluded from these deviations that the $Mo(CN)_8^{3-}$ anion exhibits slight but significant distortions from perfect dodecahedral symmetry.

In choosing the coordination polyhedron for the $Mo(CN)_8^{3-}$ anion, we examined the possibility of describing it in terms of a square antiprism of D_{4d} symmetry. However, calculation of the shape parameters clearly revealed large deviations from this symmetry. The best least-squares plane through the atoms of the proposed square face of the square antiprism is given by the equation $z = 6.842$ (Cartesian coordinates), and the deviations of the atoms from this plane are −0.24 Å for C_1 and C_1'' and 0.24 Å for C_2 and C_2''. According to its χ^2 value, the proposed square face deviates very significantly from planarity.

In the crystal, each $Mo(CN)_8^{3-}$ anion is surrounded by $(n\text{-}C_4H_9)_4N^+$ cations and the closest Mo–Mo distance is 11.39 Å. The packing, which is determined to a great extent by the $(n\text{-}C_4H_9)_4N^+$ cations, is found to be relatively loose—a conclusion supported by the extremely low density of the crystal and the observed disorder and large thermal parameters of the γ- and δ-carbon atoms of the *n*-butyl groups. A stereoscopic view of the packing is presented in Figure 2.

The $(n\text{-}C_4H_9)_4N^+$ cations have their expected tetrahedral shape, and the bond distances and bond angles for the cations are summarized in Table III. The average C–N and C–C distances in the cations are 1.57 (2) and 1.59 (2) Å, respectively. The individual cation bond distances and angles show significant deviations from the average values, principally as a result of the disorder and the consequent uncertainty in the light-atom positions. Whereas the estimated standard deviations for the anion bond distances and angles, as obtained from a function and error analysis using the variance–covariance matrix, are reasonable, the estimated standard deviations for the cation distances and angles are probably overly optimistic.

Discussion

On the basis of previous electron spin resonance studies, the $Mo(CN)_8^{3-}$ anion has been assigned a square-antiprismatic geometry in the solution state.[6,7] A compelling reason for this assignment is the relative ordering of the anisotropic g values as determined from the esr spectrum of a frozen-glass solution of $K_3[Mo(CN)_8]$. In light of the present structural results, it is clear that the assignment of the square-antiprismatic geometry for $Mo(CN)_8^{3-}$ is in need of reexamination. We have therefore measured the electron spin resonance spectrum of $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ in a polycrystalline sample and in acetonitrile solution. The results of these measurements are given in Table V along with the results reported by McGarvey for the $Mo(CN)_8^{3-}$ anion.

We find that the isotropic g value of $[(n\text{-}C_4H_9)_4N]_3$-

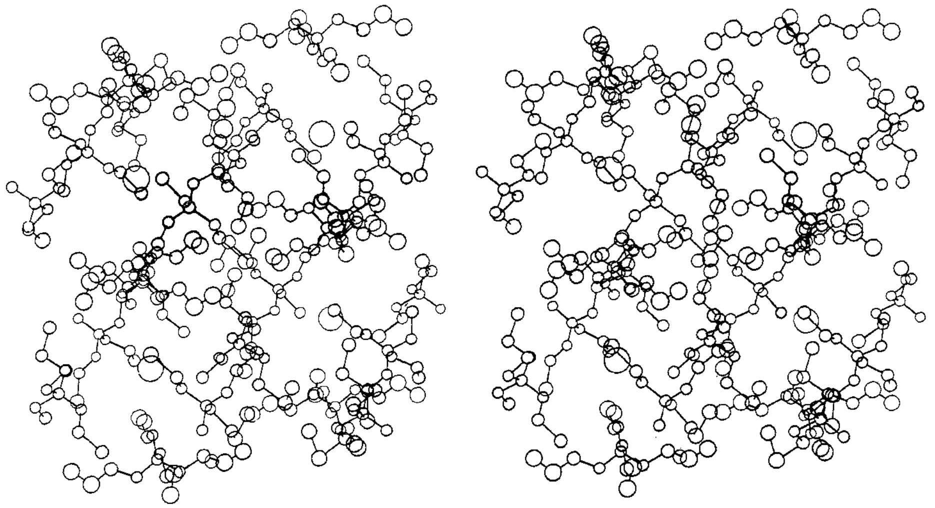

Figure 2.—A stereoscopic view of the packing as seen from a point slightly off the *a* axis of the crystal. The anions are not shown but the molybdenum positions are shown by the large circles.

[Mo(CN)$_8$] in a polycrystalline sample is equal to that obtained in acetonitrile solution and that both of these values agree well with the $\langle g \rangle$ values reported by McGarvey for $K_3Mo(CN)_8$ in an aqueous solution or calculated from a glycerine glass. Because of the equality of the isotropic *g* values determined for $Mo(CN)_8{}^{3-}$ in a variety of samples, we feel that the complex anion maintains its distorted dodecahedral coordination geometry in going from the crystalline to the solution state and that previous assignments of the square-antiprismatic geometry for the $Mo(CN)_8{}^{3-}$ anion in solution may be in error.

TABLE V

ISOTROPIC *g* VALUES AND *g*-TENSOR COMPONENTS FOR $Mo(CN)_8{}^{3-}$

Solvent	Cation	Temp, °K	$\langle g \rangle$	$g_{\parallel}$	$g_{\perp}$	Ref
H_2O	K^+	298	1.9915 (±0.0005)			6
CH_3CN	$(n\text{-}C_4H_9)_4N^+$	298	1.991 (±0.001)			This work
Glycerine	K^+	77	1.9920[a] (±0.0005)	1.9981 (±0.0005)	1.9889 (±0.0005)	6
Powder	$(n\text{-}C_4H_9)_4N^+$	298	1.991[b] (±0.001)			This work
Powder	$(n\text{-}C_4H_9)_4N^+$	100	1.991[c] (±0.001)			This work

[a] Calculated from the *g*-tensor components. [b] Measured from the resonance position of the single line in the spectrum of the polycrystalline sample. [c] Although the value of $\langle g \rangle$ at 100° does not differ from that obtained at 298°K, the line width becomes broader at lower temperatures as one would expect in a paramagnetically concentrated sample.

The ordering of the d levels for the dodecahedral geometry has been calculated to be b_2 (*xy*) > e (*xy*, *yz*) > a_1 (z_2) > b_1 ($x^2 - y^2$) while the corresponding ordering for the square-antiprismatic geometry has been found to be e (*xy*, *yz*) > e ($x^2 - y^2$, *xy*) > a_1 (z^2). Using first- and second-order perturbation theory, expressions for the spin-Hamiltonian parameters of a d^1 complex can be derived for each of these two geometries.[6] For $d_{x^2-y^2}$ as the ground-state orbital (a $^2B_1$ ground-state), one predicts that $g_{\perp}$ should be greater than $g_{\parallel}$. On the other hand, for d_{z^2} as the ground-state orbital (a $^2A_1$ ground state), one predicts that $g_{\parallel}$ should be greater than $g_{\perp}$ and that $g_{\parallel}$ should equal the free-electron value of 2.0023. The previous assignments of the square-antiprismatic structure for $Mo(CN)_8{}^{3-}$ in solution are made primarily because $g_{\parallel}$ is found to be greater than $g_{\perp}$.[6,7]

The above analysis does not consider the possibility that the coordination geometry of the anion might be intermediate between the ideal square antiprism and the ideal dodecahedron. However, a quick perusal of the available structural data on the eight-coordinate complexes indicates that it is not unusual to find complexes possessing intermediate geometries.[17] The ground-state orbital in such complexes is a linear combination of available metal and ligand functions which transform under the irreducible representation of the highest filled energy level. In the point group D_2, the true symmetry of the complex in the crystal, the choice of bonding orbitals is not as exclusive as in the two ideal cases, D_{4d} and D_{2d}. In particular, the inclusion of d_{z^2} character in the ground-state function, which is *predominantly* $d_{x^2-y^2}$, is allowed by symmetry and might lead to significant changes in the theoretical estimates of the anisotropic *g* values. It should be noted at this point that an analysis of the frozen-glass spectrum of $Mo(CN)_8{}^{3-}$ yields a value for Δg ($\Delta g = g_{\parallel} - g_{\perp}$) which

(17) See, for example, Table I of ref 16.

is much smaller than that predicted for pure D_{4d} symmetry upon theoretical considerations. The inclusion of a significant amount of d_{z^2} character in the ground-state orbital would lead to the prediction of less anisotropy in the g tensor and, hence, a smaller Δg, as well as to the correct ordering of the g-tensor components. The fact that $g_{\parallel}$ does not equal 2.0023 as predicted from theory lends further support to the idea of intermediate D_2 symmetry as well as to the notion of extensive covalent bonding.

In the final analysis, a full calculation of the anisotropic g values including both orbital mixing and covalent bonding appears necessary but beyond the scope of the present study. On the basis of the structural results and the constant isotropic g value of $Mo(CN)_8^{3-}$ in a variety of samples, we conclude that the esr parameters for this system are not indicative of the molecular geometry as predicted from crystal field considerations.

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Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. I. The Crystal Structure of $CH_3CCo_3(CO)_8P(C_6H_5)_3$

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The crystal and molecular structure of $CH_3CCo_3(CO)_8P(C_6H_5)_3$ has been determined by three-dimensional X-ray analysis. Crystals of the compound are monoclinic, space group C_{2h}^5-$P2_1/c$, with four molecules in a cell of dimensions $a = 12.19$ (2), $b = 16.11$ (2), $c = 17.19$ (4) Å; $\beta = 120.0$ (1)°. X-Ray data were collected by conventional film techniques using Co $K\alpha$ radiation, the intensities of 2189 independent reflections being measured photometrically. The structure has been refined isotropically by modified full-matrix least-squares techniques to a conventional R factor of 0.099. The monomeric molecular structure closely resembles the parent compound $CH_3CCo_3(CO)_9$ being based on a Co_3 triangle. The $P(C_6H_5)_3$ unit has simply replaced one of the *equatorial* carbonyl groups, causing small distortions in the remainder of the molecule. Co–Co bond lengths are in the range 2.490–2.510 (6) Å.

Introduction

Substituted methinyltricobalt enneacarbonyls, $YCCo_3(CO)_9$ (where Y may be halogen, alkyl, aryl, CO_2H, CF_3, etc.) are of interest for a number of reasons. First, they are very readily synthesized and have high air stability.[2] Second, they possess the unique structural feature of a tetrahedral carbon atom triply bridging a triangle of bonded metal atoms.[3] Third, there is mass spectral evidence that the Co–C bridge bonds are unusually strong.[4] Following the initial structure determination of the parent compound ($Y = CH_3$) by Sutton and Dahl,[3] the structures of $Co_3(CO)_{10}BH_2N(C_2H_5)_3$[5] and $[CCo_3(CO)_9]_2CO$[6] have been reported. Both these compounds contain the basic $-CCo_3(CO)_9$ unit as in the parent compound, with only slight distortions. Recent studies by Robinson and coworkers[7,8] indicate that methinyltricobalt enneacarbonyls undergo a number of facile chemical reactions with the production of a variety of stable products including the carbonyl carbides $Co_5(CO)_{15}C_3H$, $Co_6(CO)_{18}$-C_4, and $Co_8(CO)_{24}C_6$[9] and the complexes $YCCo_3(CO)_6$-(arene). We have undertaken a systematic study of the structures of these products and report here the first detailed results.

It has been found[7] that alkyl- and arylphosphines and -arsines react reversibly with $YCCo_3(CO)_9$ (where $Y = Cl$, Br, CH_3, C_6H_5) to give a range of complexes $YCCo_3(CO)_8L$ and $YCCo_3(CO)_7L_2$ which are air stable, volatile, and soluble without decomposition in nonpolar solvents. The solution infrared spectrum[7] of $CH_3CCo_3(CO)_8P(C_6H_5)_3$ showed bands in the bridging carbonyl region. This suggested the possibility of a rearrangement of CO groups similar to that which oc-

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(1) To whom inquiries should be addressed.

(2) For a summary of references to general properties and methods of synthesis, see B. H. Robinson and W. S. Tham, *J. Chem. Soc., A*, 1784 (1968).

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(4) See the reference cited in footnote 2.

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