tion around the aluminum atoms may be explained by considering the electrostatic repulsion between pairs of bonding electrons. Since oxygen is more electronegative than carbon, the Al–C bonding electron pairs are closer to the aluminum atom than the more strongly polarized Al–O bonding pair. Thus the C–Al–C angles become larger (116–117°) and the C–Al–O angles become smaller (100°) than the tetrahedral value. Figures 2 and 3 show the molecular structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ and packing in the crystals, respectively.

Three-coordinate oxygen is usually found in a pyramidal configuration; an exception is reported[17] for tetramethyl-O,O′-bistrimethylsilylcyclodialumoxane, where the three oxygen valencies are coplanar. In the present study, the Al–O–C(1) angle (122°) and the C(1)–O–C(1) angle (108°) are not what would be expected on the basis of sp^3 hybridization for the oxygen atoms, nor do they indicate that the oxygen is in a planar configuration.

The nmr spectra using tetramethylsilane as an internal standard indicate a chemical shift of τ 10.93 for the protons of the $(CH_3)_3Al$– group. This suggests a higher electron density at these partly negative carbon atoms than is found at the terminal carbon atoms in the trimethylaluminum dimer[18] (τ 10.67). The protons on the dioxane ring carbon atoms in the complex are in resonance at lower fields with a chemical shift of τ 6.19 compared with the protons in *p*-dioxane (τ 6.30).

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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[17] P. J. Wheatley, *J. Chem. Soc.*, 2562 (1963).

[18] N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **82**, 248 (1960).

A Compound Containing a Tetrahedral Cluster of Nickel Atoms[1]

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Abstract: The crystal structure—and simultaneously the true empirical and molecular formulas—for a compound, $Ni_4(CO)_6[P(C_2H_4CN)_3]_4$, first reported but incorrectly formulated in 1959, has been determined. The compound crystallizes in the space group $R\bar{3}$ with hexagonal unit cell dimensions $a = 18.78 \pm 0.02$ A and $c = 26.12 \pm 0.02$ A, and six formula units per cell. The molecules have nearly perfect tetrahedral symmetry aside from small deformations attributed to packing effects, although, crystallographically, only C_3 symmetry is required. In the tetrahedron of nickel atoms the mean Ni–Ni distance is 2.508 ± 0.004 A. There is a symmetrical bridging carbonyl group across each edge of the tetrahedron and a P–Ni bond collinear with each threefold axis of the tetrahedron. A qualitative discussion of the bonding would suggest that the molecule should be inherently diamagnetic. Observed paramagnetism is thus attributed to contamination by nickel metal and other magnetic impurities in bulk samples of this rather unstable substance.

Some years ago Meriwether, Colthup, Fiene, and Cotton[2] reported that the reaction of nickel carbonyl with tris(β-cyanoethyl)phosphine, $P(CH_2CH_2CN)_3$, led not only to the expected product of the $Ni(CO)_2(PR_3)_2$ type, which may be obtained with phosphines generally, but also to a red-orange product (mp 160° dec) containing less CO *and* less phosphine per metal atom. This compound, which was then formulated as $[Ni(CO)P(C_2H_4CN)_3]_n$, was found to have no infrared absorption attributable to terminal CO groups but it did exhibit one strong band at 1815 cm^{-1}. Moreover, only a single C≡N stretching band was observed at 2245 cm^{-1}, suggesting that none of the cyano groups was coordinated. It was also reported that the substance was paramagnetic, but with less than one unpaired electron per metal atom. It was suggested on the basis of this evidence that the substance was likely to be a polymer of some sort, either linear or cyclic, with the polymerization number, *n*, equal to at least 2.

In the years since this preliminary study was reported, the widespread occurrence of metal atom cluster compounds in general[3a,4] and those of the polynuclear metal carbonyl type[3b] in particular has been recognized. This prompted a reconsideration of the nature of this substance. Since it did form crystals, albeit rather unstable ones, a reinvestigation of it was undertaken using, as the principal tool, single-crystal X-ray diffraction.

As will be seen, the compound has now been shown to have the formula $Ni_4(CO)_6[P(C_2H_4CN)_3]_4$ and to contain a tetrahedral cluster of nickel atoms.

Experimental Section

Crystals of $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ were prepared by a modification of the method of Meriwether, *et al.*[2] Dry methanol (75

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[1] This work was supported, in part, by Contract No. AT(30-1)1965 with the U. S. Atomic Energy Commission.

[2] L. S. Meriwether, E. C. Colthup, M. L. Fiene, and F. A. Cotton, *J. Inorg. Nucl. Chem.*, **11**, 181 (1959).

[3] *Cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1966: (a) p 656; (b) p 719.

[4] F. A. Cotton, *Quart. Rev.* (London), **20**, 389 (1966).

ml) was distilled into a flask containing 2.9 g (0.015 mole) of tris(2-cyanoethyl)phosphine. The mixture was heated to reflux temperature, and 2.75 ml (0.022 mole) of $Ni(CO)_4$ dissolved in 50 ml of methanol was added slowly. Soon after addition of the $Ni(CO)_4$ was initiated white, crystalline $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ precipitated with evolution of CO. The reaction mixture was then allowed to stand for 24 hr at 70° after which time small orange crystals of $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ had formed. Many of the crystals grew on the surface of the magnetic stirring bar in the reaction flask. The stirring bar was carefully removed from the flask and stored in a vial under liquid nitrogen to reduce the rate of decomposition of the crystals. Suitable crystals for X-ray study were then selected from the stirring bar.

When quantities of the compound other than single crystals are desired, it is necessary to remove the $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ which is also formed in the reaction. The most satisfactory method found was to dissolve the contaminant in hot methanol, in which the cluster compound is insoluble. However, even after repeated purification, very weak bands of the impurity were still present in the infrared spectrum.

Solubility. The compound is insoluble in most organic solvents and only slightly soluble in acetonitrile and acetone. These solutions undergo slow decomposition even in the absence of ai

Infrared Spectrum. A mull spectrum of $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ in Nujol has absorption bands at 2239 (medium) and 1802 cm^{-1} (strong). They correspond to the C–N stretching frequency of the tris(2-cyanoethyl)phosphine and the C–O stretching frequency of the bridging carbonyl, respectively. Very weak bands from the $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ were also present in the spectrum.

Magnetic Properties. Magnetic measurements were made by the Gouy method. The magnetic susceptibility was measured at temperatures from 80 to 305°K and at field strengths from 2000 to 6700 oersteds. A considerable field dependence was observed over the range of field strengths, suggesting the presence of a ferromagnetic impurity. Nickel metal has been observed in the reaction flask during preparation of the compound, very likely resulting from the decomposition of $Ni(CO)_4$ or the disubstituted carbonyl. The insolubility of the compound has prevented the removal of the ferromagnetic contamination. The nonlinearity of the Curie–Weiss plot over a temperature range of 80–305°K prevents any meaningful calculation of the magnetic moment. A mean value of $\chi_g = 1.64 \times 10^{-6}$ was found at 19° which is close to that (1.8×10^{-6}) found previously.[2]

An attempt was made to determine the magnetic behavior in acetone solution by observing the proton magnetic resonances of the cyanoethyl groups, but a saturated solution was too dilute to produce an observable resonance.

Collection and Reduction of X-Ray Data. Single crystals were examined by precession photography and were found to belong to the rhombohedral system. The reflections were indexed with reference to hexagonal axes in the obverse rhombohedral setting. The space group extinctions are $-h + k + l = 3n$. The diffraction symmetry indicated the space group to be R3 (No. 146) or $R\bar{3}$ (No. 148) with unit cell dimensions $a = 18.78 \pm 0.02$ A and $c = 26.12 \pm 0.02$ A. (The rhombohedral cell dimensions are $a = 13.89$ A and $\alpha = 84.98°$.) The density measured (by flotation) in aqueous barium iodide solution is 1.45 g/cc, which agrees well with the calculated density of 1.47 g/cc for six molecules per hexagonal unit cell.

The compound was found to decompose rather rapidly on exposure to the X-ray beam, and it was therefore considered that three-dimensional data could not be satisfactorily collected by photographic methods. Initially, an attempt was made to determine heavy atom (Ni, P) positions using two-dimensional precession data from the $hk0$ and $0kl$ zones. To decrease the error introduced by decomposition of the compound, different crystals were used for collecting data from each zone. For each, a series of timed photographs was taken. However, when these data were read, it became apparent that considerable decomposition had occurred, and reduction of the data was not deemed worthwhile. The rate of decomposition of the crystals suggested, however, that a useful set of intensities could be collected by counter methods. Intensity data were thus collected at room temperature on a G.E. XRD-5 diffractometer using nickel-filtered Cu Kα radiation. The intensities were monitored with a scintillation counter with the pulse-height discriminator set for 95% with the window centered on Cu Kα radiation. Three single crystals, each in the form of a parallelepiped, were mounted with [001] parallel to the ϕ axis of the diffractometer. Reflection intensities were recorded from each crystal until the intensities of two standard reflections 0, 1, 2 and 1, 10, 0 decreased by approximately 10% of their original value, at which time a new crystal was mounted and data collection continued.

The moving crystal–moving counter method of Furnas[5] was used, but so modified that background counts were taken at the maximum and minimum values of 2θ for each scan. The diffraction characteristics of the crystals indicated that a 40-sec scan of 2.66° would adequately record the integrated intensities. The intensity of each reflection is given by the total number of counts during the scan minus the sum of the two 20-sec background counts. All independent reflections (1860) within the range $\theta_{Cu} \leq 50.4°$ were measured.

The diffractometer settings and Lorentz-polarization corrections were calculated with Shoemaker's MIXG-2 program.[6] The intensities were reduced to $|F_{hkl}|$ and $|F_{hkl}|^2$ by Elder's program, RAWRE-2.[7]

Solution of the Structure. For the purpose of calculating the Patterson function, all reflections from the three crystals were put on a single scale based upon the intensities of ten reflections which had been measured from each crystal. The possible positions of the general nickel and phosphorus atoms were found from the Harker plane (x, y, 0). Vectors from each of these nickel atoms to the nickel atom on the threefold axis indicated the presence of tetrahedral arrangements of the metal atoms and, further, that adjacent tetrahedra on a threefold axis are related by a center of symmetry.

It was not apparent from the Patterson map that the phosphorus atoms were also related by a center of symmetry, since vectors between center-related phosphorus atoms were either much weaker than other phosphorus–phosphorus vectors or did not appear. However, after a series of trial-and-error Fourier electron-density maps phased on the nickel atoms and an incomplete set of phosphorus atoms had been studied, it was seen that each phosphorus atom was actually related to another by a center of symmetry. Two successive difference Fourier maps then revealed the positions of all the remaining atoms and indicated that the proper space group was $R\bar{3}$. The subsequent successful refinement of the structure has substantiated this choice.

A structure factor calculation based on the atom positions found from the difference Fourier map had the residuals

$$R_1 = \frac{\Sigma \big| |F_o| - |F_c| \big|}{\Sigma |F_o|} = 0.272$$

$$R_2 = \left[\frac{\Sigma \omega [|F_o| - |F_c|]^2}{\Sigma \omega |F_o|^2}\right]^{1/2} = 0.273$$

For the refinement, all reflections were rejected for which $\sqrt{(P + B)}/(P - B) > 0.5$, where P is the number of counts measured during the scan, and B is the total background count. Of a total of 1860 reflections measured, 843 were rejected using the above criterion.

The atom coordinates, three scale factors, and isotropic atomic thermal parameters were refined by a full-matrix, least-squares procedure, minimizing $\Sigma\omega[|F_o| - |F_c|]^2$. Atomic-scattering factors for neutral Ni, P, C, N, and O used are those given by Ibers.[8] The real and imaginary terms for Ni and P[9] arising from anomalous dispersion were included in calculating the structure factors.[10]

No correction was made for absorption of X-rays by the crystals, since μr_{max} was less than 0.15 ($\mu = 18.7$ cm^{-1} for Cu Kα radiation).

After four cycles of isotropic least-squares refinement, the residuals R_1 and R_2 decreased to 0.114 and 0.133, respectively. Since a unit weighting scheme has little justification in practice, an attempt was made to introduce a scheme more closely related to the experiment in which the weight, ω, of each reflection is approximated by the expression $[0.95 - 0.195|F_o'| + 0.008|F_o'^2|]^{-1}$. Applying this expression, another cycle of refinement resulted in values of $R_1 = 0.107$ and $R_2 = 0.127$. The weighting scheme was then checked by plotting $[|F_o| - |F_c|]^2$ as a function of $|F_o|$. It was found that the weighting scheme would be more satisfactorily

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(5) T. G. Furnas, Jr., "Single Crystal Orienter Instruction Manual," X-ray Department, General Electric, Schenectady, N. Y., 1957.

(6) D. P. Shoemaker, "MIXG-2, M.I.T. X-ray Goniometer Package," 1962.

(7) R. C. Elder, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

(8) J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(9) C. H. Dauben and D. H. Templeton, ref 8, p 214.

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

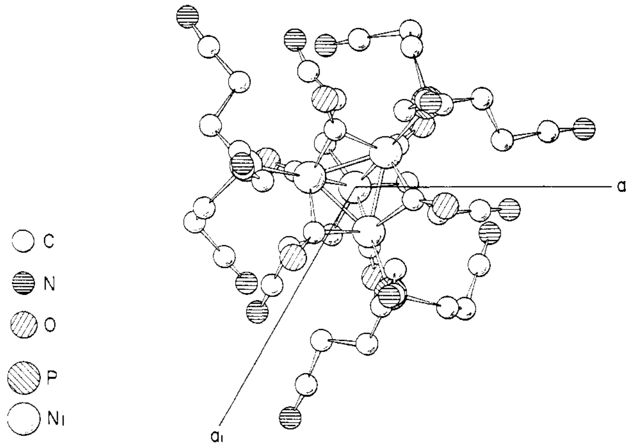

Figure 1. A projection of the $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ molecule down the *c* axis. (Due to an oversight, the P atom at the left is not shaded.)

estimated by $|F_o'| \leq 12.0$, $\omega = 12/(66.9 - 4.10|F_o|)$; $|F_o'| > 12.0$, $\omega = 12/(3.3 + 1.15|F_o'|)$. In the expressions for the weight of a reflection, F_o' is related to the structure amplitude on an absolute scale, $|F_o|$, by $|F_o'| = {}^1/_3|F_o| \times$ (scale factor). A further cycle of refinement produced $R_1 = 0.107$ and $R_2 = 0.112$.

In order to determine the effect of crystal decomposition on the data, the reflections were grouped according to the crystal from which each was obtained. Each group was then used separately as data for a cycle of refinement in which only the scale factor and an over-all temperature factor B_0 were allowed to vary. The initial value of B_0 was set at 2.0 A², which also was subtracted from each atomic thermal parameter. The initial and final values of the parameters are shown in Table I. The small divergence in the three over-all temperature factors indicates that the effect of decomposition was practically equivalent for the three crystals, and it is clear from the behavior of the scale factors that no compensation was necessary to bring the three sets of data to a common scale other than individual scale factors.

Table I. Refinement of Over-all Temperature Factor and Scale Factor for Data Sets from Three Crystals

	B_0, A²		Scale factor	
Crystal	Initial	Final	Initial	Final
1	2.00	1.98	0.232	0.232
2	2.00	2.04	0.281	0.283
3	2.00	1.97	0.307	0.306

The final cycle of refinement using all the data produced no change in the residuals: $R_1 = 0.107$, $R_2 = 0.112$. The largest parameter shift in the last cycle was ¹/₄th of its estimated standard deviation. The largest feature on a difference Fourier map calculated from the final atom positions was a peak of 1.2 e/A³ near atom C(8). This together with the high temperature factors and poor bond lengths associated with atoms C(7) and C(8) suggest some disorder in this cyanoethyl chain.

The final atomic positional and thermal parameters and their estimated errors are listed in Table II. The estimated standard deviations were calculated from the usual least-squares formula, $\sigma^2(j) = a_{jj}(\Sigma\omega\Delta^2)/(m - n)$, where a_{jj} is the appropriate element of the matrix which is inverse to the normal equation matrix. The observed and calculated structure amplitudes times 12 are listed in Table III.

Fourier and least-squares programs used in the calculations were MIFR-2A, a modification of Sly, Shoemaker, and Van den Hende's Fourier program,[11] and Prewitt's full-matrix least-squares crystallographic program SFLSQ-3.[12]

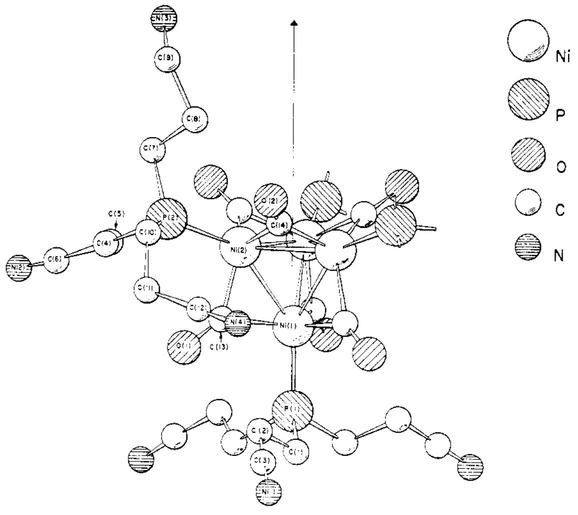

Figure 2. A perspective view of the $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ molecule. Numbering of atoms corresponds to that in Tables II and IV–VI.

Description of the Structure

A crystal of $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ is composed of distinct molecules stacked along the threefold axis of the space group with adjacent molecules in the stack related by a center of symmetry.

Table II. Final Atom Coordinates and Thermal Parameters[a]

Atom	*X/a*	*Y/b*	*Z/c*	*B*, A²
Ni(1)	0.0	0.0	0.21778 (18)	2.9 (1)
Ni(2)	0.08495 (16)	0.06592 (16)	0.29606 (11)	3.0 (1)
P(1)	0.0	0.0	0.13493 (31)	3.2 (2)
P(2)	0.20235 (30)	0.15951 (31)	0.32556 (20)	3.6 (1)
C(1)	−0.0066 (11)	0.0841 (11)	0.1012 (6)	4.2 (4)
C(2)	0.0513 (11)	0.1675 (11)	0.1254 (7)	4.2 (4)
C(3)	0.0451 (14)	0.2313 (14)	0.0995 (9)	6.2 (6)
C(4)	0.2978 (15)	0.1704 (16)	0.2982 (9)	7.6 (6)
C(5)	0.2913 (18)	0.0895 (18)	0.2929 (11)	9.5 (7)
C(6)	0.3764 (15)	0.1067 (21)	0.2741 (12)	11.1 (10)
C(7)	0.2249 (15)	0.1571 (15)	0.3916 (9)	7.2 (6)
C(8)	0.1582 (19)	0.1457 (19)	0.4235 (13)	10.0 (8)
C(9)	0.2025 (31)	0.1668 (30)	0.4820 (22)	17.6 (17)
C(10)	0.2305 (11)	0.2688 (11)	0.3195 (7)	4.2 (4)
C(11)	0.2321 (12)	0.2977 (12)	0.2651 (8)	4.8 (4)
C(12)	0.1501 (14)	0.2821 (13)	0.2487 (8)	5.4 (5)
C(13)	0.1136 (11)	0.0825 (11)	0.2260 (7)	4.2 (4)
C(14)	0.0234 (13)	0.1101 (13)	0.3247 (8)	5.6 (5)
N(1)	0.0425 (13)	0.2811 (14)	0.0750 (8)	8.8 (6)
N(2)	0.4375 (20)	0.1114 (18)	0.2635 (11)	12.6 (8)
N(3)	0.2084 (18)	0.1622 (18)	0.5218 (13)	12.2 (8)
N(4)	0.0878 (13)	0.2701 (11)	0.2360 (7)	6.7 (5)
O(1)	0.1721 (8)	0.1204 (8)	0.1991 (5)	5.3 (3)
O(2)	0.0360 (7)	0.1686 (7)	0.3504 (5)	4.2 (3)

[a] Numbers in parentheses are estimated standard deviations and occur in the last significant figure for each parameter.

The closest intermolecular contacts are between cyanoethyl chains of neighboring molecules. The shortest of these, 3.21 A, is between the nitrogen atom of one chain and a methylene carbon atom of another. All contacts up to 4.5 A have been calculated,[13] and pertinent values are listed in Table IV.

A projection of the complete molecule down the *c* axis is shown in Figure 1. A perspective drawing, in

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[11] 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.

[12] C. T. Prewitt, "A Full-Matrix Crystallographic Least Squares Program for the IBM 709/7090," 1962.

[13] D. P. Shoemaker, "DISTAN-Crystallographic Bond Distance, Bond Angle, and Dihedral Angle Program," 1963.

Table III. Observed and Calculated Structure Amplitudes Times 12

H	K	FOBS	FCAL
****L = 0******			
3	0	1200	1043
6	0	999	1068
9	0	512	375
12	0	1413	1287
1	1	6892	7183
4	1	1457	1325
7	1	793	411
10	1	1006	873
13	1	1525	1484
5	2	3291	3412
11	2	741	1093
14	2	901	755
3	3	1078	913
6	3	386	97
9	3	2052	1922
1	4	7213	7098
4	4	429	698
7	4	1334	1358
2	5	5157	5028
5	5	499	269
8	5	707	616
3	6	1052	1134
6	6	807	670
1	7	2132	1677
4	7	1207	1102
7	7	1005	507
2	8	2601	2507
5	8	1360	1656
8	8	1080	1065
3	9	4879	4722
6	9	1598	1651
9	9	973	509
1	10	3599	3257
4	10	3144	3240
2	11	3150	3073
5	11	1698	1711
3	12	2456	2298
1	13	1436	1556
4	13	1292	1582
2	14	1295	1154
****L = 1******			
1	0	1789	1862
4	0	3782	4209
7	0	2293	2318
10	0	962	742
16	0	833	336
2	1	3889	3397
5	1	2672	2474
8	1	3616	3480
0	2	110	164
3	2	2324	2669
6	2	3470	3462
9	2	1600	1695
1	3	2547	2846
-2	3	293	94
4	3	3917	4060
7	3	2078	1880
10	3	728	1181
-1	4	1320	1422
2	4	2096	1976
5	4	3714	3816
0	5	1145	1286
3	5	2056	2327
-3	5	659	449
6	5	2095	1808
9	5	989	670
12	5	1066	1078
1	6	777	757
-2	6	704	479
4	6	3298	3631
-5	6	1532	1611
10	6	978	1002
-1	7	1257	1087
2	7	900	916
-4	7	461	524
0	8	1674	1718
-3	8	1970	1799
-6	8	236	624
-2	9	2613	2658
4	9	615	335
-5	9	1301	1263
-8	9	3557	3863
-1	10	540	526
-4	10	1898	1862
5	10	872	897
-7	10	385	141
0	11	1113	1024
-3	11	1356	1114
-6	11	759	847
-9	11	949	786
-2	12	1712	1743
-1	13	1465	1376
-4	13	801	663
5	13	684	151
-7	13	971	1054
-10	13	1056	890
-3	14	1147	1167
-6	14	836	738
1	15	844	413
-2	15	894	732
-5	15	1432	1239
-4	16	1706	1614
-6	17	1814	2066
-5	18	1496	1614
-8	18	822	700
****L = 2******			
2	0	5690	5958
5	0	2642	2234
8	0	2049	1847
11	0	844	615
14	0	971	748
0	1	7602	7999
3	1	6492	6102
6	1	1091	1011
1	2	4182	4173
4	2	1168	1296
7	2	1714	1537
-1	3	340	739
2	3	2229	2526
5	3	873	583
8	3	1925	1768
0	4	388	356
3	4	2369	2016
-3	4	352	432
6	4	1072	965
9	4	1016	878
1	5	379	438
-2	5	2843	2689
4	5	3694	3521
10	5	956	830
13	5	1044	902
-1	6	857	848
2	6	2063	1981
-4	6	372	347
5	6	762	914
8	6	783	8
11	6	1275	1270
0	7	756	980
3	7	2376	2415
-3	7	2699	2596
-6	7	1794	1789
1	8	1365	985
-2	8	969	908
4	8	1743	1587
-5	8	440	71
7	8	865	602
-1	9	2132	2092
2	9	2874	2919
-4	9	2532	2383
5	9	911	1954
0	10	1527	1550
3	10	2623	2802
-3	10	2001	2103
6	10	971	1106
-6	10	765	655
-9	10	1776	1739
1	11	1309	1414
4	11	2243	2367
-5	11	443	227
-8	11	1978	1937
-1	12	1867	1728
2	12	1157	1067
-7	12	1819	1715
-10	12	2753	2719
-6	13	974	949
-9	13	2662	2784
-12	13	1844	1966
-8	14	1451	1422
-11	14	1992	2040
-1	15	900	751
2	15	959	795
-10	15	1564	1572
-13	15	1424	1454
-3	16	987	927
-12	16	1225	1193
-5	17	1110	1049
-11	17	908	851
-14	17	898	746
-13	18	888	834
****L = 3******			
0	0	6663	6430
3	0	709	576
6	0	2924	3100
9	0	2710	2728
12	0	1007	714
1	1	813	531
4	1	4564	4645
7	1	3053	2930
10	1	1438	1423
13	1	1118	807
2	2	1018	1422
8	2	2085	1900
0	3	144	307
3	3	5631	5308
6	3	3319	3560
9	3	1293	1264
1	4	653	545
-2	4	838	691
4	4	4502	4393
7	4	1830	1815
10	4	1369	1587
13	4	897	453
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5	5	2091	2077
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-3	6	1713	1458
6	6	1193	995
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-1	8	1307	1290
-4	8	1053	931
-7	8	1698	1563
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-8	10	416	116
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-7	11	429	236
-10	11	557	211
-9	12	1593	1630
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5	1	615	536
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-5	6	2362	2420
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-4	7	2119	2067
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-6	8	2761	2644
9	8	1063	1077
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5	6	925	1097
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-6	7	1631	1543
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-3	10	1179	949
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14	2	1767	1488
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5	5	802	972
8	5	761	758
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-4	8	2356	2193
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-7	8	981	752
8	8	1275	1420
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-6	9	2692	2968
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6	2	2473	2470
9	2	1035	806
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-1	4	627	130
2	4	480	253
5	4	1300	1398
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6	5	1463	1333
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-5	6	850	756
7	6	859	932
-1	7	793	707
2	7	565	494
-4	7	413	71
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-5	9	1163	1062
-8	9	535	699
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5	10	1695	1580
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3	11	1538	1531
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-8	12	1237	1250
-11	12	1069	1082
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-12	14	1849	1863
-5	15	1066	996
-14	15	897	974
-4	16	799	762
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-1	6	2889	3202
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-3	7	2792	3053
9	7	1502	1566
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-2	8	2318	2403
4	8	1031	1025
-5	8	1711	1732
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-1	9	1951	2097
2	9	2218	2256
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-6	10	1809	1785
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-2	4	887	882
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-1	5	414	36
2	5	860	886
-4	5	414	419
5	5	1143	1141
8	5	789	426
3	6	2211	2289
-3	6	797	769
4	7	1628	1686
-5	7	707	437
-1	8	1118	1216
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-7	8	693	828
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6	9	1396	1339
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-1	11	1387	1425
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5	11	1534	1692
-10	11	790	847
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3	12	1613	1789
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-8	13	2083	2183
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-7	14	1164	1150
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3	5	1596	1600
-3	5	2124	2262
6	5	654	651
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-2	6	1916	2005
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-5	6	1274	1403
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-1	7	2280	2344
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-5	9	931	825
-8	9	746	771
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-7	10	677	549
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-9	11	1228	1151
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2	3	770	1149
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2	6	1660	1351
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-1	9	743	781
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-1	12	899	652
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-7	12	1147	1008
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3	3	2178	1886
6	3	1789	2060
9	3	1061	830
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4	4	1956	2140
7	4	1570	1542
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-5	7	2653	2808
-4	8	720	561
-7	8	676	340
-2	10	1285	1059
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-4	11	877	981
-3	12	1269	1165
-4	14	1268	1224
-6	15	1187	1060
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5	1	2730	3092
8	1	1228	1154
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3	2	833	682
6	2	2648	2849
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-4	7	955	847
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-3	8	2197	2213
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-4	10	1031	997
-7	10	881	1096
-4	13	1064	1003
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7	2	1108	1067
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2	3	612	40
8	3	804	893
3	4	903	1061
6	4	1313	1263
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-6	7	1247	1206
-2	8	1327	1291
-5	8	1142	1192
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3	10	968	603
-3	10	1589	1871
-6	10	630	11
-5	11	1061	1184
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1	1	866	946
7	1	1473	1710
2	2	880	690
5	2	2135	2334
8	2	1293	1355
0	3	618	396
3	3	911	1096
6	3	2475	2770
4	4	1417	1677
5	5	1191	928
0	6	660	876
-3	6	838	542
6	6	977	288
-2	7	1757	1753
-1	8	880	1036
-4	8	1455	1517
-7	8	722	284
-3	9	970	1173
-7	11	906	732
****L = 19******			
5	1	815	679
-2	3	1228	1223
0	5	1318	1184
-2	6	1090	1305
-1	7	965	1208
-4	7	1236	1219
-3	8	1483	1530
-2	9	1205	1390
-4	10	1396	1364
****L = 20******			
5	0	1651	1549
6	1	979	1087
1	2	804	876
7	2	1396	1543
-1	3	934	560
5	3	1289	1260
3	4	1184	1302
6	4	1468	1582
1	5	1176	1216
2	6	976	850
-4	6	788	865
-6	7	1217	1027
-3	10	900	909
****L = 21******			
0	0	1052	617
-1	2	778	382
0	3	825	443
-1	5	1192	1006
0	6	1092	1109
-3	6	1198	1121
-2	7	1844	1955
-1	8	987	939
-4	8	1454	1643
-3	9	1065	1215
-5	10	894	893
****L = 22******			
1	0	963	670
8	1	882	895
-2	3	797	566
-2	6	1066	883
4	6	1067	816
-4	7	1210	1276
-3	8	1334	1636
-2	9	1051	1418
-8	9	888	883
-4	10	678	927
****L = 23******			
2	0	1092	955
0	1	976	700
-2	5	1140	1372
-1	6	1063	1098
-2	8	1119	1270
****L = 24******			
6	0	832	515
-1	2	1066	900
3	3	838	634
0	6	832	496
-2	7	1181	1423
****L = 25******			
2	1	1083	901
-2	3	1324	1416
-1	4	1431	1398

which six of the cyanoethyl chains are omitted for clarity, is presented in Figure 2. The intramolecular bond lengths and bond angles[14] and their estimated standard deviations are listed in Tables V and VI. The molecule contains a tetrahedral cluster of nickel atoms with phosphorus-bonded tris(β-cyanoethyl)phosphine ligands at the apices and bridging carbonyl groups at the edges of the tetrahedron. The space group requires the molecule to have threefold symmetry, but it is only slightly distorted from tetrahedral symmetry with the exception of the arrangement of the cyanoethyl chains of the phosphine ligands.

Each nickel atom interacts with seven neighboring atoms forming bonds with three nickel atoms, three carbon atoms, and one phosphorus atom. The average nickel–nickel bond length is 2.508 ± 0.004 A, and the values of the two crystallographically independent types differ by an amount (0.0056 A) of the order of only one estimated standard deviation. Consequently, within experimental error the nickel atom cluster has undistorted tetrahedral symmetry.

The average nickel–phosphorus bond length is 2.161 ± 0.005 A, and the tetrahedral symmetry is slightly distorted by the phosphorus atoms. The interatomic distance between phosphorus atoms related by the threefold axis is 6.008 ± 0.011 A, and the distance from one of these to the phosphorus atom on the threefold axis is 6.067 ± 0.008 A; thus there is a slight elongation of the tetrahedron composed of phosphorus atoms. Since there is no apparent chemical reason for it, this distortion is assumed to be due to intermolecular forces in the crystal. The tetrahedral symmetry of the molecule is further destroyed by the arrangement of the cyanoethyl chains. Those attached to the phosphorus atom in the special position (on the threefold axis) are related by the threefold axis. However, those on the three phosphorus atoms which occupy general positions have no internal symmetry. Thus the chain composed of atoms C(10), C(11), and C(12) folds back toward the molecule, while the other two

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[14] J. S. Wood, "MGEOM, A Molecular Geometry Program for the IBM 7094," Massachusetts Institute of Technology, 1964.

Table IV. Intermolecular Contacts

	Atom in given molecule	Atom (2) in neighboring molecule	Coordinates of atom (2) relative to those of same atom in given molecule	Interatomic distance, A
1	C(1)	N(2)	$(y - {}^1/_3, {}^1/_3 + y - x, {}^1/_3 - z)$	3.64
2	C(1)	N(2)	$({}^2/_3 - x, {}^1/_3 - y, {}^1/_3 - z)$	3.94
3	C(2)	N(2)	$({}^2/_3 - x, {}^1/_3 - y, {}^1/_3 - z)$	3.30
4	C(3)	N(2)	$({}^2/_3 - x, {}^1/_3 - y, {}^1/_3 - z)$	3.63
5	C(4)	N(1)	$({}^2/_3 + x - y, {}^1/_3 + x, {}^1/_3 - z)$	3.54
6	C(4)	N(1)	$({}^2/_3 - y, {}^1/_3 + x - y, {}^1/_3 + x)$	3.92
7	C(5)	C(10)	$({}^1/_3 + x - y, x - {}^1/_3, {}^2/_3 - z)$	3.91
8	C(5)	N(1)	$({}^2/_3 - y, {}^1/_3 + x - y, {}^1/_3 + z)$	3.47
9	C(6)	N(1)	$({}^2/_3 - y, {}^1/_3 + x - y, {}^1/_3 + z)$	3.52
10	C(6)	C(10)	$({}^1/_3 + x - y, x - {}^1/_3, {}^2/_3 - z)$	3.93
11	C(7)	N(1)	$({}^2/_3 - y, {}^1/_3 + x - y, {}^1/_3 + z)$	3.77
12	C(7)	N(2)	$({}^1/_3 + y, {}^2/_3 + y - x, {}^2/_3 - z)$	3.85
13	C(8)	N(3)	$(y, y - x, 1 - z)$	3.91
14	C(8)	N(3)	$(x - y, x, 1 - z)$	3.21
15	C(9)	C(9)	$(x - y, x, 1 - z)$	3.64
16	C(9)	N(3)	$(x - y, x, 1 - z)$	3.40
17	C(9)	C(8)	$(y, y - x, 1 - z)$	3.87
18	C(9)	N(3)	$(y, y - x, 1 - z)$	3.68
19	C(10)	C(12)	$({}^1/_3 - x, {}^2/_3 - y, {}^2/_3 - z)$	3.75
20	C(10)	N(4)	$({}^1/_3 - x, {}^2/_3 - y, {}^2/_3 - z)$	3.68
21	C(10)	O(2)	$({}^1/_3 - x, {}^2/_3 - y, {}^2/_3 - z)$	3.84
22	C(10)	N(1)	$({}^2/_3 + y - x, {}^1/_3 + x, {}^1/_3 - z)$	3.59
23	C(11)	N(3)	$({}^1/_3 + y - x, {}^2/_3 - x, z - {}^1/_3)$	3.32
24	C(11)	O(2)	$({}^1/_3 - x, {}^2/_3 - y, {}^2/_3 - z)$	3.58
25	C(11)	N(1)	$({}^2/_3 + x - y, {}^1/_3 + x, {}^1/_3 - z)$	3.21
26	C(12)	N(3)	$({}^1/_3 + y - x, {}^2/_3 - x, z - {}^1/_3)$	3.40
27	N(1)	N(2)	$({}^1/_3 + y - x, {}^2/_3 - x, z - {}^1/_3)$	3.88
28	N(2)	O(1)	$({}^2/_3 - x, {}^1/_3 - y, {}^1/_3 - z)$	3.76
29	N(3)	N(3)	$(y, y - x, 1 - z)$	3.74
30	N(3)	N(4)	$({}^2/_3 - y, {}^1/_3 + x - y, {}^1/_3 + z)$	3.85
31	N(3)	O(2)	$(x, y - x, 1 - z)$	3.40

Table V. Bond Distances[a]

	Bond	Distance, A		Bond	Distance, A
1	Ni(1)-Ni(2)	2.506 (5)	14	P(2)-C(10)	1.852 (19)
2	Ni(2)-Ni(2)′	2.512 (6)	15	C(1)-C(2)	1.53 (3)
3	Ni(1)-C(13)	1.922 (18)	16	C(4)-C(5)	1.47 (4)
4	Ni(2)-C(13)	1.889 (19)	17	C(7)-C(8)	1.43 (4)
5	Ni(2)-C(14)	1.881 (22)	18	C(10)-C(11)	1.52 (3)
6	Ni(2)′-C(14)	1.852 (22)	19	C(2)-C(3)	1.43 (3)
7	Ni(1)-P(1)	2.163 (10)	20	C(5)-C(6)	1.54 (5)
8	Ni(2)-P(2)	2.161 (6)	21	C(8)-C(9)	1.69 (7)
9	C(13)-O(1)	1.194 (23)	22	C(11)-C(12)	1.48 (3)
10	C(14)-O(2)	1.206 (25)	23	C(3)-N(1)	1.16 (3)
11	P(1)-C(1)	1.866 (19)	24	C(6)-N(2)	1.14 (5)
12	P(2)-C(4)	1.844 (25)	25	C(9)-N(3)	1.05 (7)
13	P(2)-C(7)	1.783 (25)	26	C(12)-N(4)	1.12 (3)

[a] Numbers in parentheses are the estimated standard deviations and occur in the last significant figure of each bond length.

chains extend out from the nickel cluster. The arrangement of the carbon chains appears to be the result of interatomic repulsions, particularly those between the C(10), C(11), C(12) chain of one molecule and that composed of atoms C(1), C(2), C(3), and N(1) located at $({}^2/_3 + x - y, {}^1/_3 + x, {}^1/_3 + z)$ in the neighboring molecule. Atom N(1) approaches within 3.21 A of C(11) in the folded chain.

Bond angles involving atoms Ni-P-C(α) and C(α)-P-C′(α) have been calculated and are shown in Table VI. The average Ni-P-C(α) angle is 118.7 ± 0.4°, which is within the range, 114–120°, commonly found in complexes of coordinated phosphines. The average C(α)-P-C′(α) angle is 98.5 ± 0.6°.

Table VI. Bond Angles, Degrees

Atoms forming angle			Angle, deg	Est std dev
Ni(2)	Ni(1)	Ni(2)′	60.15	0.17
Ni(1)	Ni(2)	Ni(2)′	59.93	0.09
Ni(2)	Ni(1)	P(1)	144.64	0.32
Ni(1)	Ni(2)	P(2)	146.22	0.18
Ni(2)′	Ni(2)	P(2)	143.00	0.20
Ni(2)′′	Ni(2)	P(2)	145.01	0.20
Ni(1)	C(13)	Ni(2)	82.2	0.7
Ni(1)	C(13)	O(1)	137.4	1.5
Ni(2)	C(13)	O(1)	140.3	1.5
Ni(2)	C(14)	Ni(2)′	84.6	0.9
Ni(2)	C(14)	O(2)	137.6	1.7
Ni(2)′	C(14)	O(2)	137.8	1.7
Ni(1)	P(1)	C(1)	118.1	0.7
Ni(2)	P(2)	C(4)	119.5	0.8
Ni(2)	P(2)	C(7)	118.9	0.8
Ni(2)	P(2)	C(10)	118.7	0.6
P(1)	C(1)	C(2)	111.0	1.2
P(2)	C(4)	C(5)	110.4	1.8
P(2)	C(7)	C(8)	111.5	1.9
P(2)	C(10)	C(11)	114.8	1.3
C(1)	C(2)	C(3)	110.5	1.6
C(4)	C(5)	C(6)	105.7	2.4
C(7)	C(8)	C(9)	101.5	2.9
C(10)	C(11)	C(12)	111.5	1.6
C(2)	C(3)	N(1)	174.2	2.4
C(5)	C(6)	N(2)	171.9	3.4
C(8)	C(9)	N(3)	158.9	4.8
C(11)	C(12)	N(4)	179.6	2.2
P(1)	Ni(1)	C(13)	96.4	0.6
P(2)	Ni(2)	C(13)	96.9	0.6
P(2)	Ni(2)	C(14)	95.8	0.7
P(2)	Ni(2)	C(14)′′	96.9	0.7
C(1)	P(1)	C(1)′	99.6	0.9
C(4)	P(2)	C(7)	98.5	1.1
C(7)	P(2)	C(10)	99.8	1.0
C(10)	P(2)	C(4)	97.0	1.0

The bond lengths found between other atoms of the cyanoethyl groups are close to those expected with the exception of that group composed of atoms C(7), C(8), C(9), and N(3), which shows evidence of disorder. Thus the bond lengths and errors calculated for these atoms are not considered reliable.

There is no evidence that any coordination of the nickel atoms by nitrogen occurs. The closest nickel–nitrogen distance is 4.12 A between N(4) and Ni(2).

The bridging carbonyl groups are symmetrical; each carbon atom is equidistant, within experimental uncertainty, from each of the two nickel atoms to which it is bonded. The mean of these Ni–C distances is 1.890 ± 0.003 A. This figure is similar to those found in other cases, *e.g.*, in dicobalt octacarbonyl[15] (1.92 ± 0.01 A) and $[(C_5H_5)Fe(CO)_2]_2$[16] (1.85 ± 0.03 A). The average carbon-to-oxygen distance, 1.20 ± 0.02 A, is quite comparable to those[15,16] (1.20 ± 0.02, 1.21 ± 0.04 A) found in similar cases.

Ideally, that is, for perfect tetrahedral symmetry, the six carbon atoms and the six oxygen atoms would each define a regular octahedron. There is, however, minor distortion which takes the form of a slight bending of some of the CO groups out of the plane defined by the two nickel atoms to which they are bonded and the midpoint of the opposite edge of the tetrahedron of

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[15] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, **17**, 732 (1964).

[16] O. S. Mills, *ibid.*, **11**, 620 (1958).

nickel atoms. Only the three carbonyl groups bound to the nickel atom on the crystallographic threefold axis show this distortion which appears to arise from the close contact of O(1) with the methylene group containing C(11). These two atoms are separated by only 3.40 A, which is just equal to the sum of the van der Waals radii.[17]

Discussion

The structure found in this compound is significant since it is only the third authenticated example of a metal atom cluster containing a virtually regular tetrahedral array of metal atoms. The other tetrahedral clusters are found in $(\pi\text{-}C_5H_5)_4Fe_4(CO)_4$, in which there is a triply bridging CO group on each face and the Fe–Fe distances have a mean value of 2.516 A,[18] and $Ir_4(CO)_{12}$, which has no bridging carbonyl groups.[19]

There are, of course, a number of similar though less symmetrical molecules, including the nickel compound, $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$, which has an equilateral triangle of Ni atoms[20] with nickel–nickel bond lengths of 2.39 ± 0.007 A, which is significantly shorter than that determined here.

Other transition metal clusters and their metal–metal distances which may be compared with the nickel tetrahedron are: $Co_4(CO)_{12}$ (2.49 + 0.02 A),[19] $[Fe_4(CO)_{13}]^{2-}$ (2.58 ± 0.005 and 2.50 ± 0.006 A),[21] $Co_3(CO)_9CCH_3$ (2.467 ± 0.007 A),[22] and $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ (2.43 and 2.55 A).[23] The distance in nickel metal is 2.492 A.[24]

The structure is consistent with the presence of only a single CO stretching band in the bridging region of the infrared spectrum. In rigorous tetrahedral molecular symmetry, which is closely approximated in the crystal, the normal modes due to the set of six CO oscillators would belong to the A_1, E, and T_2 representations of the group T_d. Only the T_2 mode is infrared active.

This molecule, with its high symmetry, affords an excellent opportunity for investigating the bonding involved in the type of metal atom cluster compound which occurs in many polynuclear metal carbonyls. A formulation of the electronic structure in terms of molecular orbitals is desirable but lengthy. Prior to the completion of such a treatment, it will be useful to discuss the bonding in terms of a purely qualitative formulation involving only two-center, two-electron bonds. Such a formulation is possible in this instance although this is not always the case.[25]

The nine valence-shell orbitals of each metal atom ($4s$, $4p^3$, $3d^5$) may be used to construct a set of hybrid orbitals in the local symmetry (C_{3v}) of each metal atom. The basis for doing this is summarized in Table VII. Three types of hybrid orbitals are required: (type A) one σ orbital directed toward the phosphorus atom; (type B) three equivalent σ orbitals directed toward the carbonyl carbon atoms; (type C) three equivalent σ orbitals directed toward the other three nickel atoms.

Table VII. Symmetry Properties of Metal Orbitals

Symmetry type, C_{3v}	Metal orbitals	No. of orbitals required for each type of hybrid		
		A	B	C
A_1	$4s$, $3d_{z^2}$, $4p_z$	1	1	1
A_2				
E	$(p_x,p_y)(d_{xz},d_{yz})(d_{xy},d_{x^2-y^2})$		1	1

It is clear from Table VII that atomic orbitals of the requisite symmetry classes are available to form these hybrids, and, thereafter, a pair of E orbitals will remain.

One may now assume that the A orbital on each nickel atom remains vacant until utilized to form the P→Ni donor bond. One nickel electron should then be placed in each of the B orbitals so that covalent bonds can be formed to the carbon atoms. Finally, each of the C orbitals should be allotted one electron so that a set of six Ni–Ni single bonds may be formed.

In the preceding paragraph, six electrons and seven of the nine valence-shell orbitals of each nickel atom have been accounted for. There remain then four electrons and two (E-type) orbitals. The four electrons can be assigned to these two remaining orbitals. Thus, with this simple picture, we arrive at an electronic structure which has the following salient features: (1) it accounts for all the two-center bonds which the structure requires; (2) it suggests that the Ni–Ni bonds are essentially single bonds, although the unspecified nature of the E orbitals which are occupied by the "nonbonding" electrons leaves this somewhat uncertain; (3) it implies that the molecule has a closed-shell structure and should, therefore, be diamagnetic.

An obvious question which remains unanswered in this simple analysis is why a molecule such as this has been isolated only with the particular phosphine, tris(β-cyanoethyl)phosphine. It may be that analogs can be made with other phosphines under suitable conditions. On the other hand, tris(β-cyanoethyl)phosphine possesses a most unusual combination of low steric requirements and very low basicity.[26] The low basicity arises from the electron-withdrawing character of the cyano groups, and there may be associated with this an enhanced ability of phosphorus to use its d orbitals to accept dπ electrons from the metal. If this is so, the special stability of this type of compound with this particular phosphine might be due to its capacity to withdraw electron density from the nominally nonbonding E-type orbitals. It might be that in the absence of such an effect these electrons would exert an antibonding influence on the Ni_4 cluster. If this is true, one might expect that analogous compounds

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(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(18) M. A. Neuman, R. B. King, and L. F. Dahl, unpublished studies.

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(20) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The MacMillan Co., New York, N. Y., 1961, p 640.

(21) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

(22) P. W. Sutton and L. F. Dahl, *ibid.*, **89**, 261 (1967).

(23) L. F. Dahl and D. L. Smith, *ibid.*, **84**, 2450 (1962).

(24) "Tables of Interatomic Distances and Configuration of Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(25) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963), discuss $Rh_6(CO)_{16}$, for which such a description is at best ambiguous.

(26) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

containing $(RO)_3P$ and F_3P (and perhaps even CO) in place of $(NCC_2H_4)_3P$ might be stable enough to be isolated.

A final point requiring discussion is the observed paramagnetism of the compound in bulk as contrasted with the indication from the discussion of bonding that the compound should have no unpaired electrons. In view of the instability of the compound, the observation of visible traces of nickel metal in some preparations, field-strength dependence of the observed magnetism, and the lack of correspondence of the observed magnetism with any integral number of electrons, we believe it is safe to attribute the observed magnetism to the presence of nickel metal and perhaps also paramagnetic decomposition products.

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Chromatographic Resolution of the Antipodes of a Helical Complex of Nickel(II)

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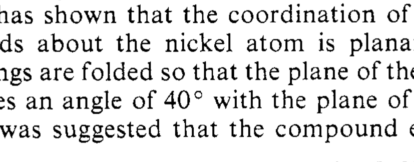
Abstract: Chromatographic resolution of the complex ion triaquotribenzo[*b,f,j*][1,5,9]triazacycloduodecinenickel(II), $Ni(TRI)(H_2O)_3^{2+}$, has been achieved on microcrystalline cellulose and on potato starch. Fractional crystallization of partially resolved samples reveals that the chromatographic resolutions are essentially complete. This first separation of enantiomeric complexes on cellulose shows this to be a very convenient and useful material for such procedures. (+)- or (−)-$Ni(TRI)(H_2O)_3^{2+}$ does not racemize at a measurable rate in acidic or neutral solutions; however, the complex is unstable in aqueous base. The chirality of the complex may be assigned on the basis of the natural helical form of the molecule with respect to the C_3 axis. Circular dichroism spectra and optical rotatory dispersions are reported.

Although early attempts were made to resolve $Ni_2(trien)_3^{4+}$ [2,3] and $Ni(en)_3^{2+}$ [4,5] into optical isomers, the first successful separation of a dissymmetric nickel(II) complex into antipodal forms involved tris-(2,2′-bipyridine)nickel(II).[6] The resolution of this material was initially accomplished by crystallizing the *d*- or *l*-tartrate salt. Racemization of $Ni(bipy)_3^{2+}$ proceeds with a half-life of 2.5 min in aqueous solution at 30°. The rate of racemization is accelerated by both acid and base.[7] Tris(1,10-phenanthroline)nickel(II) was resolved at a later date[8] and found to racemize much more slowly. Its racemization half-life is 2 hr in aqueous solution at 30° and the rate is almost independent of pH. In 1962 Broomhead and Dwyer prepared and resolved the related ions $[Ni(bipy)_2(phen)]^{2+}$ and $[Ni(bipy)(phen)_2]^{2+}$.[9] These enantiomers, like $[Ni(bipy)_3]^{2+}$, racemize rapidly in aqueous solution at rates that are accelerated by both acid and base. The diamagnetic complex shown in structure I has been partially resolved by preferential adsorption of one enantiomorph on (+)-quartz.[10,11] The asymmetry of this complex was attributed to distortion of the planar structure toward a "quasi-tetrahedral" arrangement. A recent X-ray determination of the structure of this complex has shown that the coordination of the nitrogen ligands about the nickel atom is planar, but the chelate rings are folded so that the plane of the formazyl ring makes an angle of 40° with the plane of coordination. It was suggested that the compound exists as a



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[1] National Institutes of Health Postdoctoral Fellow, 2-F2-GM-28, 091-02.

[2] tren is the abbreviation for tris(aminoethyl)amine $N(CH_2CH_2NH_2)_3$.

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