Preparation, Structure, and Bonding of a New Type of Metal Cluster System, $[M_2Ni_3(CO)_{16}]^n$ (M = Cr, Mo, W; $n = -2$): A Nonconformist to the Noble Gas Metal Society

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Abstract: A novel reaction between nickel tetracarbonyl and the dinuclear metal decacarbonyl anions of chromium, molybdenum, and tungsten has produced a new kind of transition metal atom cluster system, $[M_2Ni_3(CO)_{16}]^n$ (M = Cr, Mo, W; $n = -2$), which has been mainly isolated and characterized as bis(triphenylphosphine)iminium salts (where the monocation is abbreviated as PPN). These relatively air-stable, diamagnetic complexes of chromium, molybdenum, and tungsten were shown from the close similarity of their infrared spectra to have the same basic geometry for the three common $[M_2Ni_3(CO)_{16}]^{2-}$ anions each possessing a different group VI element. The ionic nature of $[PPN]_2[W_2Ni_3(CO)_{16}]$ as a 1:2 electrolyte was demonstrated from conductivity studies. The detailed atomic parameters of the anion have been unambiguously established from three-dimensional X-ray diffractometry investigations of $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$, $[PPN]_2[Mo_2Ni_3(CO)_{16}]$, and $[PPN]_2[W_2Ni_3(CO)_{16}]$, which revealed the unprecedented example of a trigonal-bipyramidal arrangement of bonding transition metal atoms. The configuration of the $[M_2Ni_3(CO)_{16}]^{2-}$ anion may be ideally described in terms of a planar $Ni_3(CO)_6$ residue (containing three identical Ni(CO) fragments positioned at the vertices of an equilateral triangle and connected to one another by bridging carbonyl groups and Ni–Ni interactions) of D_{3h}-$\bar{6}2m$ geometry symmetrically coordinated to two identical apical $M(CO)_5$ groups, each of localized C_{4v}-$4mm$ site symmetry, by only direct Ni–M interactions; the two $M(CO)_4$ groups are stereochemically oriented relative to the $Ni_3(CO)_6$ fragment such that (based on an assumed D_{3h} geometry for the M_2Ni_3 cluster system) the entire anion approximately possesses C_{2v}-$2mm$ symmetry. A molecular orbital description of the bonding is presented, in which each $M(CO)_5$ group is considered to be bonded to a cyclopropenyl-like trinickel ring system which occupies one coordination site. The proposal that each $M(CO)_5$ group is primarily coordinated to the three nickel atoms by only one delocalized electron-pair bond not only is in accord with the observed Mo–Ni and W–Ni distances of average value 3.10 Å, which is 0.3 Å longer than a presumed normal electron-pair single-bond Mo–Ni or W–Ni distance but also is consistent with certain degradation reactions of $[PPN]_2[W_2Ni_3(CO)_{16}]$ which fragments to give $[W_2(CO)_{10}]^{2-}$ or $[W(CO)_5Cl]^-$ anions. The MO model invoked also rationalizes the nonconformity of the $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W) to the noble gas configuration for each metal atom and the observed distortion of the M_2Ni_3 cluster system from D_{3h} to C_{3v} geometry. It leads to electron-pair nickel–nickel bonds, which is not inconsistent with the observed nickel–nickel internuclear distances of average value 2.34 Å in both the $[Mo_2Ni_3(CO)_{16}]^{2-}$ and $[W_2Ni_3(CO)_{16}]^{2-}$ anions. The $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$ salt crystallizes with eight formula species in a monoclinic unit cell of dimensions $a = 24.124$ (12) Å, $b = 12.083$ (4) Å, $c = 28.888$ (11) Å, and $\beta = 88.785$ (22)° and of symmetry $C2/c$. Although the crystal structural analysis of this compound resolved the geometry of the crystallographically independent anion (except for the two tungsten-attached apical carbonyl carbon atoms), intensive efforts to locate the two independent tetraethylammonium cations were unsuccessful presumably due to their being disordered in the large cavities formed by the packing of the anions. The $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ salt and the isomorphous $[PPN]_2[W_2Ni_3(CO)_{16}]$ salt crystallizes in the triclinic system with $a = 14.307$ (7) Å, $b = 15.230$ (7) Å, $c = 10.964$ (5) Å, $\alpha = 91.557$ (7)°, $\beta = 105.500$ (6)°, and $\gamma = 62.985$ (6)° for the molybdenum compound and $a = 14.361$ (2) Å, $b = 15.299$ (2) Å, $c = 11.014$ (2) Å, $\alpha = 91.658$ (4)°, $\beta = 105.482$ (4)°, and $\gamma = 62.943$ (4)° for the tungsten compound. The crystal-disordered model successfully utilized in the least-squares refinements assumes that the average unit cell containing one formula species possesses centrosymmetric $P\bar{1}$ symmetry such that the one $[M_2Ni_3(CO)_{16}]^{2-}$ anion (M = Mo, W) is located on an average center of symmetry with the two PPN cations per cell related to each other by the center of symmetry. Hence, the crystal disorder necessarily requires the $Ni_3(CO)_6$ residue of each anion to appear as two crystallographically related orientations of half-weighted atoms with the two $M(CO)_5$ fragments centrosymmetrically related to each other. The resulting six half-weighted nickel atoms form a disordered six-pronged star arrangement about the centrosymmetric origin in the triclinic cell in a manner similar to the "Star of David" centrosymmetric-disordered arrangement found to occur for the two isosceles triangles of six half-weighted iron atoms in the crystal-disordered structure of $Fe_3(CO)_{12}$. Full-matrix least-squares refinement with anisotropic thermal parameters for the metal and phosphorus atoms and isotropic ones for all other atoms and with the six phenyl groups in the $[PPN]^+$ cation each constrained to its well-known geometry resulted in final discrepancy factors of $R_1 = 6.0\%$ and $R_2 = 6.5\%$ for 2240 observed data of the molybdenum compound and of $R_1 = 4.2\%$ and $R_2 = 5.7\%$ for 2375 observed data of the tungsten compound.

Since 1957 when metal–metal bonds *per se* were shown from X-ray diffraction investigations[3,4] to stabilize several dimeric transition metal carbonyl complexes, a wide variety of polynuclear transition metal complexes containing metal–metal bonds have been synthesized and structurally characterized.[5–9] Al-

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(3) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27, 809 (1957).

(4) L. F. Dahl, E. Ishishi, and R. E. Rundle, *ibid.*, 26, 1750 (1957); L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

though a considerable number of new types of metal cluster systems containing two, three, four, six, and (greater than six)[10,11] transition metal atoms have been established, the only pentanuclear transition metal cluster system reported previously[12] is the $Fe_5(CO)_{15}C$ molecule, which was shown from an X-ray examination[13] to possess a bonding tetragonal pyramid of iron atoms together with a unique pentacoordinated carbon atom positioned slightly below the basal plane of four iron atoms at essentially equal bond distances from each of the five iron atoms. This paper reports the isolation and stereochemistry of a second type of pentanuclear transition metal cluster which was synthesized from a novel reaction between the dinuclear metal decacarbonyl anions[14-17] of chromium, molybdenum, and tungsten with nickel tetracarbonyl.

Although an earlier study[18] showed that these anions are useful intermediates in the preparation of mixed-metal derivatives such as $CrCo(CO)_9^-$ and $CrMn(CO)_{10}^-$, no species containing more than two metal atoms was isolated prior to this investigation. However, treatment of the dinuclear chromium, molybdenum, and tungsten carbonyl anions with nickel carbonyl yielded mixed metal cluster anions which, when isolated as bis(triphenylphosphine)iminium salts, were initially presumed from elemental chemical analyses to contain 3 (or 4) nickel atoms and 2 group VI metal atoms along with 16 carbonyl groups. The ionic nature of the tungsten compound as a 1:2 electrolyte was indicated from conductivity studies. Proton nmr of the tungsten and molybdenum compounds showed the absence of hydridic hydrogen atoms as well as paramagnetic impurities. The diamagnetism of these tungsten and molybdenum salts at room temperature was confirmed from magnetic susceptibility measurements by the Faraday method.[19] The very similar infrared spectra of the chromium, molybdenum, and tungsten compounds indicated the same basic metal cluster structure for the $[M_2Ni_3(CO)_{16}]^{2-}$ anions. The unambiguous formulation of the anion as a $[M_2Ni_3(CO)_{16}]^{2-}$ species was made possible by X-ray studies of the molybdenum and tungsten complexes which revealed the first known example of a trigonal-bipyramidal metal framework.

Experimental Procedure

Preparation and Properties of $\{[(C_6H_5)_3P]_2N\}_2[M_2Ni_3(CO)_{16}]$ where M = Cr, Mo, and W) and $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$. The preparation of all three group VI metal derivatives was carried out in an analogous manner. Hence, only the preparation of the tungsten compound is given. A flask containing a mixture of 8.7 g of $\{[(C_6H_5)_3P]_2N\}_2[W_2(CO)_{10}]$[20] in 200 ml of freshly distilled THF was attached to a conventional vacuum line and degassed. Then, 24 mmol of $Ni(CO)_4$ (measured by PVT means) was condensed into the mixture in the flask. The reaction was allowed to warm to ambient temperature. Upon being filled with nitrogen gas, the flask was removed from the vacuum line and attached to a reflux condenser, after which the mixture was refluxed under N_2 atmosphere for 1.5 hr. The solvent subsequently was removed under vacuum and 150 ml of CH_2Cl_2 was added to the resulting residue. The mixture was filtered and ethyl acetate (100 ml) was added to the filtrate. For $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$, a 7.1-g sample (yield based on tungsten was 68%) was obtained as orange crystals of mp 191–193° dec. The corresponding yields varied from approximately 30% for the chromium derivative to about 60% for the molybdenum analog. The melting point for $\{[(C_6H_5)_3P]_2N\}_2[Cr_2Ni_3(CO)_{16}]$ is 221–223° dec, while the melting point for $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$ is 198–200° dec.

Anal. Calcd for $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$: W, 17.77; Ni, 8.51; P, 5.99; O, 12.37; N, 1.35; C, 51.08; H, 2.92. Found: W, 17.7; Ni, 10.9; O, 12.1; N, 1.40; C, 50.0; H, 2.82. Calcd for $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$: Mo, 10.13; Ni, 9.30; P, 6.54; O, 13.52; N, 1.48; C, 55.83; H, 3.19. Found: Mo, 9.6; Ni, 11.7; O, 12.9; N, 1.50; C, 54.4; H, 3.18. Calcd for $\{[(C_6H_5)_3P]_2N\}_2[Cr_2Ni_3(CO)_{16}]$: Cr, 5.76; Ni, 9.76; P, 6.86; O, 14.18; N, 1.55; C, 58.54; H, 3.35. Found: Cr, 5.6; Ni, 12.7; O, 13.7; N, 1.50; C, 56.7; H, 3.22.

These salts, which are all relatively stable, vary in color from orange for the tungsten to dark red for the chromium compound. The tungsten and molybdenum compounds are the most stable and may be handled in air with no apparent decomposition occurring even after several months. The least stable chromium derivative is also the most difficult to isolate in pure form.

The tetramethylammonium salt of the $[W_3Ni_3(CO)_{16}]^{2-}$ anion, obtained in a similar manner by the reaction of $[(CH_3)_4N]_2[W_2(CO)_{10}]$ and $Ni(CO)_4$ in THF, was isolated and recrystallized from a THF–CH_2Cl_2–ether mixture.

Anal. Calcd for $[(CH_3)_4N]_2[W_2Ni_3(CO)_{16}]$: W, 32.25; Ni, 15.45; O, 22.45; N, 2.46; C, 25.28; H, 2.12. Found: W, 29.89; O, 22.74; N, 2.65; C, 24.8; H, 2.26.

The infrared spectra of bis(triphenylphosphine)iminium salts of tungsten, molybdenum, and chromium were taken in CH_2Cl_2 solutions with a Perkin-Elmer Model 621 grating spectrometer (calibrated with indene) at concentrations of approximately 0.010 m*M* in a 0.1-mm sodium chloride cell. The following absorption bands were recorded in the carbonyl stretching region: for $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$ 2036 (w), 1998 (s), 1930 (mw), 1896 (s), 1835 (m), and 1791 (w) cm^{-1}; for $[(C_6H_5)_3P]_2N_2[Mo_2Ni_3(CO)_{16}]$ 2039 (w), 1994 (s), 1933 (m), 1901 (s), 1838 (m), and 1786 (w) cm^{-1}; for $\{[(C_6H_5)_3P]_2N_2\}[Cr_2Ni_3(CO)_{16}]$ 2040 (w), 1982 (s), 1925 (w), 1890 (m), 1842 (mw), and 1795 (w) cm^{-1}.

The conductivity of the $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$ salt was determined as a function of concentration in nitromethane solutions with equipment previously described.[21] The specific conductance ($ohm^{-1}\ cm^{-1}$) of the nitromethane solvent employed was 6.31×10^{-7}. The concentration (*M*) and corresponding equivalent conductance ($cm^2\ ohm^{-1}\ equiv^{-1}$) for various solutions are: 4.868×10^{-3}, 60.5; 2.434×10^{-3}, 66.0; 1.217×10^{-3}, 71.2; 6.085×10^{-4}, 77.5; 3.042×10^{-4}, 79.6. A plot of equivalent conductance Λ *vs.* $(\text{concentration})^{1/2}$ gives a limiting value of the equivalent conductance Λ_0 at infinite dilution of $85 \pm 1\ cm^2\ ohm^{-1}\ equiv^{-1}$, while the slope of the plot, $(\Lambda_0 - \Lambda)$ *vs.* $(\text{concentration})^{1/2}$ is approximately 420; this latter value is not inconsistent with a 1:2 electrolyte in nitromethane.[22]

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(5) M. C. Baird, *Progr. Inorg. Chem.*, 8, 1 (1968), and references contained therein.

(6) P. Chini, *Inorg. Chim. Acta Rev.*, 2, 31 (1968), and references contained therein.

(7) B. R. Penfold in "Perspectives in Structural Chemistry," Vol. II, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1968, p 71.

(8) F. A. Cotton, *Accounts Chem. Res.*, 2, 240 (1969), and references contained therein.

(9) E. W. Abel and F. G. A. Stone, *Quart. Rev., Chem. Soc.*, 23, 325 (1969), and references contained therein.

(10) V. G. Albano, P. L. Bellon, and G. F. Ciani, *Chem. Commun.*, 1024 (1969); P. Chini and S. Martinengo, *ibid.*, 1092 (1969).

(11) V. G. Albano and P. L. Bellon, *J. Organometal. Chem.*, **19**, 405 (1969); P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 299 (1969).

(12) The pentameric mercapto cobalt carbonyl complex $Co_5(CO)_{10}(SC_2H_5)_5$ is comprised not of a pentanuclear cobalt cluster system but instead of a basic triangular metal cluster $M_3X_6Y_3$ system of stoichiometry $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ which is coordinated by two of its thioethyl ligands to the cobalt atoms of a $Co_2(CO)_5(SC_2H_5)$ fragment which possesses the $Fe_2(CO)_6(SC_2H_5)_2$-type geometry: C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **90**, 3969 (1968).

(13) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *ibid.*, 84, 4633 (1962).

(14) E. Lindner, H. Behrens, and S. Birkle, *J. Organometal. Chem.*, **15**, 165 (1968), and references contained therein.

(15) U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965).

(16) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Amer. Chem. Soc.*, 88, 366 (1966); R. G. Hayter, *ibid.*, 88, 4376 (1966), and references cited therein.

(17) W. C. Kaska, *ibid.*, **90**, 6340 (1968); **91**, 2411 (1969).

(18) J. K. Ruff, *Inorg. Chem.*, 7, 1818 (1968).

(19) We are indebted to Mr. Michael Camp of the University of Wisconsin (Madison) for carrying out these magnetic measurements for us.

(20) J. K. Ruff, *Inorg. Chem.*, 6, 2080 (1967).

(21) J. K. Ruff, *ibid.*, 2, 813 (1963).

(22) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Reactions of $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$. (a) Decomposition to $\{[(C_6H_5)_3P]_2N\}[W(CO)_5Cl]$. The degradation of the tungsten–nickel cluster system to give the $[W(CO)_5Cl]^-$ anion was found to occur either by a redox reaction with $HgCl_2$ or by irradiation in CH_2Cl_2 solution.

$\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$, 1 g, in 25 ml of THF was treated with 0.4 g of $HgCl_2$ in 5 ml of THF for 0.5 hr at ambient temperature. Ether (50 ml) was added to the mixture, which was then filtered. Pentane was added to the filtrate, and upon cooling a 0.71-g sample of $\{[(C_6H_5)_3P]_2N\}[W(CO)_5Cl]$ was obtained. After recrystallization from a CH_2Cl_2–ether–pentane mixture the product was identified by comparison of infrared spectra and by mixture melting point. No nickel was found to be present by analysis.

A 0.5-g sample of $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$ in 25 ml of CH_2Cl_2 was irradiated in a Pyrex vessel with an AH-4 lamp for 15 min. The solution changed from red to yellow color, and an off-white solid was deposited. Ether (50 ml) was added to the reaction mixture, which was then filtered. Upon addition of pentane to the filtrate, a 0.4-g sample of $\{[(C_6H_5)_3P]_2N\}[W(CO)_5Cl]$ was obtained. The product was identified as described above.

(b) Reaction with Carbon Monoxide. A 1-g sample of $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$ in 25 ml of THF was allowed to react with an excess of CO (approximately 25 atm) in a pressure reactor. The mixture was held at 90° for 3 hr. Upon cooling, an orange-yellow-colored solid precipitated. This residue was removed by filtration and found to consist of 0.75 g of $\{[(C_6H_5)_3P]_2N\}_2[W_2(CO)_{10}]$. The product was identified by comparison of infrared spectra and by mixture melting point.

When the same quantities of reactants were allowed to react in CH_2Cl_2 under photolytic activation at ambient temperature, only a trace amount of $\{[(C_6H_5)_3P]_2N\}_2[W_2(CO)_{10}]$ was obtained. The major product was $\{[(C_6H_5)_3P]_2N\}[W(CO)_5Cl]$.

Attempted Reactions. Attempts to protonate the $[W_2Ni_3(CO)_{16}]^{2-}$ anion in THF solution with 85% phosphoric acid were not successful. Neither triphenylphosphine nor the cyanide anion, as $\{[(C_6H_5)_3P]_2N\}CN$, reacted with the $[W_2Ni_3(CO)_{16}]^{2-}$ anion in refluxing THF (over a 3-hr period).

Single-Crystal X-Ray Data Collection of $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$, $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$, and $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$. Samples with crystals suitable for X-ray analysis were obtained by recrystallization procedures not only for $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ and $[PPN]_2[W_2Ni_3(CO)_{16}]$ (where PPN represents the bis(triphenylphosphine)iminium cation, $[(C_6H_5)_3P]_2N^+$) but also for $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$. Several crystals of each compound were cemented to the end of glass fibers and characterized by oscillation, Weissenberg, and precession photographs.

The tetraethylammonium salt of the tungsten complex was chosen first for study because a solution of its structure was thought to require less computer time owing to the fewer atoms involved and because it was thought to be the analog of another partially solved structure, $[(C_2H_5)_4N]_2[Mo_2Ni_4(CO)_{14}]$.[23] Crystals were transferred from Weissenberg and precession cameras to a General Electric four-circle automated diffractometer. Each of the crystals was optically and then X-ray aligned, and 10–20 reflections (see Table I) were carefully centered.[24] The lattice constants (20°) obtained by least-squares refinement[25] were used to generate the angle settings for all data reflections.[26] All intensity data were collected at a takeoff angle of 2.0° by the θ–2θ scan technique. Symmetric 2θ scans of 2.00° were taken at 2.00°/min. Stationary-crystal–stationary-counter background counts of 15.0 sec were taken at the beginning and end of each scan. Four standard reflections were measured after every 100 reflections. After the collection of 800 reflections, a 50% decrease of the intensity of the standards was noted. A larger needle-shaped crystal mounted about the b axis was chosen for the second attempt to collect intensity data; the first set of data was considered completely useless and was discarded. The second crystals was substantially (but not sufficiently) more stable, and collection of 2000 reflections took place with a 50% decrease in the intensity of the standards. After correction for decay by use of the four standard reflections, the intensities were corrected for background and Lorentz–polarization effects;[27] a $\sigma(I)$ was calculated for each reflection, with an "ignorance" factor empirically assigned the value 0.0016.[28] A reflection was considered "observed" if the intensity, I, was greater than $2\sigma(I)$. For Mo Kα radiation the linear absorption coefficient of 73.4 cm^{-1} necessitated a correction for absorption.[29] While the data from the second crystals were used to solve for the positions of the metal atoms, a third plate-like crystal mounted about the c axis was transferred to the diffractometer. The intensities of the standard reflections decreased by 10% during the collection of the hkl and $\bar{h}kl$ intensity data but decreased by 40% during the collection of $\bar{h}k\bar{l}$ and $hk\bar{l}$ intensity data. The third set of data was treated as described above. The geometrical shape of the third crystal was used to correct for absorption.[29,30] The data were merged[31] if the observations for the twofold related reflections were within a $3\sigma(I)$ range; both were discarded from all further calculations if they were not within this range.

The crystals used to collect intensity data of $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ and $[PPN]_2[W_2Ni_3(CO)_{16}]$ were found to be mounted about the $(0,\bar{1},1)$ axis of the reduced cell[32] of a primitive triclinic lattice. The crystals of the tungsten compound and later the molybdenum compound were transferred to the diffractometer. Each of the crystals was optically and then X-ray aligned, and 20 reflections were carefully centered.[24] The lattice constants (20°) obtained by a least-squares refinement[25] were used to generate the angle settings

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[23] A preliminary X-ray examination (W. R. Costello and L. F. Dahl, unpublished research) of crystals of the tetraethylammonium salt of a reaction product between the $[Mo_2(CO)_{10}]^{2-}$ anion and $Ni(CO)_4$ (prepared by J. K. Ruff) has revealed another new kind of metal cluster system of apparent composition $[(C_2H_5)_4N]_2[Mo_2Ni_4(CO)_{14}]$. The crystals of this salt are orthorhombic with eight formula species in a unit cell of lattice lengths a = 11.961 (7), b = 23.421 (15), c = 31.701 (20) Å, and of space group symmetry $Fddd$(D_{2h}^{24}, no. 70). A solution of the crystal structure, obtained both from combined Patterson–Fourier syntheses and from symbolic addition analysis of film- and diffractometry-collected intensity data, established a mixed-metal Mo_2Ni_4 cluster system. Its geometry may be considered to arise from two bonding trinickel triangles being fused along a common triangular edge to give a diamond-shaped planar arrangement of four nickel atoms, each of which is coordinated to the two molybdenum atoms disposed perpendicularly above and below the centroid of the planar tetranickel fragment. The crystallographic site symmetry of the anion is D_2-222, with the two symmetry-related molybdenum atoms located on one twofold axis, one pair of crystallographically equivalent nickel atoms located on another twofold axis, and the other pair of different type nickel atoms located on the third intersecting twofold axis. Although an apparent disordering of the tetraethylammonium cations has prevented a least-squares refinement to date of the crystal structure, the observed peaks about the Mo_2Ni_4 metal framework appear to correspond to: (1) each of the two molybdenum atoms possessing four terminal carbonyl groups; (2) each of the one pair of related nickel atoms, which are coordinated to each other as well as to the other pair of nickel atoms, possessing two terminal carbonyl groups coplanar with the tetranickel plane and symmetry related by the twofold axis passing through the attached nickel atoms; (3) each of the other pair of nickel atoms, which are bonded only to their two adjacent nickel neighbors, possessing one terminal carbonyl group coplanar with the tetranickel plane and lying on the twofold axis which passes through their bonded nickel atoms. The resulting $[Mo_2Ni_4(CO)_{14}]^{2-}$ anion ideally possesses D_{2h}-$2/m2/m2/m$ symmetry. The localized environment about each of one pair of equivalent nickel atoms may be considered as a symmetrically deformed pentagonal bipyramid, while the bonding environment about each of the other two equivalent nickel atoms may be regarded as a distorted trigonal bipyramid. Each of the two eight-coordinated molybdenum atoms has a square-antiprismatic-like arrangement of four carbonyl groups and four nickel atoms about it. This molecular configuration is in accord with a closed-shell electronic configuration for each of the three types of metal atoms. Further work is in progress to ascertain these preliminary X-ray findings.

[24] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Company, Milwaukee, Wis., 1957.

[25] A. S. Foust, "A Method for Calculation of Lattice and Orientation Parameters of a Crystal Mounted on a Four-Circle Diffractometer," Ph.D. Thesis, University of Wisconsin (Madison), 1970.

[26] ANGSET, a local modification of "Orientation and Angle Setting General Program," Program B-101, Argonne National Laboratory, 1965.

[27] DREDGE, a local Fortran program for diffractometer data reduction, University of Wisconsin (Madison), 1967.

[28] V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3756 (1969).

[29] J. F. Blount, DEAR, an absorption-correction program based on the method of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

[30] Details of the absorption correction for each crystal, including the characterization of the normal of each crystal face in terms of the Eulerian angles χ and ϕ, together with the perpendicular distances from a common origin inside the crystal to the faces are given in the Ph.D. thesis of R. P. White, Jr., University of Wisconsin, 1970.

[31] J. F. Blount, INTAV, an intensity averaging program based on the method of A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[32] S. L. Lawton and R. A. Jacobson, "The Reduced Cell and Its Crystallographic Applications," IS-1141, Ames Laboratory of the U. S. Atomic Energy Commission, Iowa State University, Ames, Iowa, 1965.

for all data reflections.[26] All intensity data were collected at a take-off angle of 6.0° for the tungsten compound and of 5.0° for the molybdenum compound by the θ–2θ scan technique. Symmetric 2θ scans of 1.90° for the tungsten and 2.20° for the molybdenum compound were taken at 2.00°/min. Stationary-crystal–stationary-counter background counts of 13.5 sec for the tungsten complex and 16.5 sec for the molybdenum complex were taken at the beginning and end of each scan. Zirconium-filtered Mo Kα radiation was employed with a scintillation detector followed by a pulse-height analyzer adjusted to accept 90% of the Mo Kα pulse distribution. Intensity data (hkl, $\bar{h}kl$, $h\bar{k}l$, $hk\bar{l}$) were collected twice for $2\theta < 35°$ and once for 2θ between 35 and 45°. Four standards, measured every 100 reflections during the entire data collection, were used to correct the intensities of the tungsten compound for a slight decay (5% on intensity). All reflections greater than 10,000 counts/sec were recollected with an attenuated X-ray beam and scaled up with the use of the four standard reflections. Correction for slight movements of the tungsten crystal was made by a centering of eight reflections every 48 hr and a fitting of these angle settings to the lattice parameters. The resulting orientation parameters were used to generate the angle settings for the subsequent 48 hr. For those reflections measured twice the intensities were compared, and in the case of disagreement by greater than $3\sigma(I)$ both measurements were deleted from subsequent calculations. For the tungsten compound only the first observation was used for a reflection due to a higher rate of decay during the time of the second measurement. For the molybdenum compound the observations were averaged, because there was neither decay nor movement of the crystal. The intensities were corrected for background and Lorentz-polarization effects,[27] and $\sigma(I)$'s were calculated with an ignorance factor empirically assigned the value 0.0025.[28] A reflection was considered observed if the intensity, I, was greater than $2\sigma(I)$. A total of 4235 and 4757 observed independent reflections resulted from this procedure for the molybdenum and tungsten compounds, respectively. For Mo Kα radiation the linear absorption coefficients, given in Table I for both compounds, necessitated a correction for absorption.[29, 30] The transmission factors varied from 0.312 to 0.650 for the tungsten compound and from 0.533 to 0.797 for the molybdenum analog. Real and imaginary dispersion corrections[33] for Mo Kα radiation were applied for molybdenum ($\Delta f' = -1.7$, $f'' = 0.9$) and tungsten ($\Delta f' = -1.0$, $\Delta f'' = 8.0$), but the relatively small values of these corrections for Ni ($\Delta f' = 0.4$, $\Delta f'' = 1.2$) and for P ($\Delta f' = 0.1$, $\Delta f'' = 0.2$) were presumed not to have any significant effect on the atomic coordinates in these centrosymmetric crystals[34] and hence were not used in least-squares refinements. The scattering factors used for the nonhydrogen atoms are those compiled by Hanson, *et al.*,[35] while the hydrogen scattering factors are those of Stewart, *et al.*[36]

Crystal Data. The least-squares-calculated lattice constants (20°) and estimated standard deviations[25] for the monoclinic cell of $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$ as well as the experimental and calculated densities are recorded in Table I. The observed systematic absences of $h + k = 2n + 1$ for $\{hkl\}$ data and $l = 2n + 1$ for $\{h0l\}$ data indicate that the probable space group is either $Cc(C_s{}^4$, no. 9)[37] or $C2/c(C_{2h}{}^6$, no. 15).[38] With the space group initially assumed to be the centrosymmetric one, $C2/c$, a solution of the structure would require the location of 2 tungsten, 3 nickel, 16 oxygen, 2 nitrogen, and 32 carbon atoms corresponding to one formula species as the crystallographically independent unit.

The least-squares-calculated lattice constants (20°) and estimated standard deviations[25] for the reduced triclinic unit cell of $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$ and $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$ are given in Table I.

The experimental density of 1.67 g/cm³ (flotation method) agrees well with the value of 1.66 g/cm³ calculated on the basis of one of the formula species, $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$, per cell. Similarly, for the molybdenum analog the observed density is 1.50 g/cm^{-3} and the calculated density is 1.54 g/cm^{-3}. The lack of systematic absences is in accord with a primitive lattice for the above reduced cell parameters. The space group was initially assumed to be $P1(C_1{}^1$, no. 1)[39] rather than $P\bar{1}(C_i{}^1$, no. 2),[40] because the anion by itself does not possess a center of symmetry. This was later shown not to be the case due to a crystal disorder such that the average unit cell of symmetry $P\bar{1}$ has the one $[M_2Ni_3(CO)_{16}]^{2-}$ anion located on an average center of symmetry with the two PPN cations per cell related to each other by the center of symmetry. Hence, for the anion the solution of the structure required the location of three half-weighted nickel atoms, six half-weighted carbon atoms, and six half-weighted oxygen atoms, comprising the $Ni_3(CO)_6$ fragment randomly oriented in one of two centrosymmetrically related positions together with the molybdenum (or tungsten) atom, and five whole-weighted carbon and whole-weighted oxygen atoms comprising the $M(CO)_5$ fragment. The determination of the atomic coordinates of the PPN cation required the location of one nitrogen and two phosphorus atoms along with six phenyl rings.

Table I. Crystallographic Data for $\{[(C_6H_5)_3P]_2N\}_2[M_2Ni_3(CO)_{16}]$ (M = Mo, W) and $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$

	$\{[(C_6H_5)_3P]_2N\}_2[M_2Ni_3(CO)_{16}]$ M = Mo	$\{[(C_6H_5)_3P]_2N\}_2[M_2Ni_3(CO)_{16}]$ M = W	$[(C_2H_5)_4N]_2$-$[W_2Ni_3(CO)_{16}]$
a, Å	14.307 (7)	14.361 (2)	24.124 (12)
b, Å	15.230 (7)	15.299 (2)	12.083 (4)
c, Å	10.964 (5)	11.014 (2)	28.888 (11)
α, deg	91.557 (7)	91.658 (4)	90 (. . .)
β, deg	105.500 (6)	105.482 (4)	88.785 (22)
γ, deg	62.985 (6)	62.943 (4)	90 (. . .)
Volume, Å³	2038.5	2064.7	8418.4
d_{obsd}, g/cm³ [a]	1.50	1.67	2.03
d_{calcd}, g/cm³	1.54	1.66	1.98
Z	1	1	8
μ, cm^{-1} [b]	11.2	38.7	73.4
Transmission (min)	0.533	0.312	0.232
Transmission (max)	0.797	0.650	0.446
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
n[c]	20	20	16
m[d]	2240	2375	
mt[e]	4235	4757	2322
Data-to-parameter ratio	10.8	11.5	
R_1[f] for data of range $10 \leq 2\theta \leq 35$, %	6.0	4.2	
R_2[g] for data of range $10 \leq 2\theta \leq 35$, %	6.5	5.7	
R_1[f] for all data, %	7.1	5.1	
R_2[g] for all data, %	9.3	6.3	
Takeoff angle	5.0	6.0	2.0
Scan range, deg	2.2	1.9	2.0
Background count time, sec	16.5	13.5	15.0

[a] d_{obsd} = density measured by flotation in monobromobenzene for the molybdenum compound, in mixtures of tetrachloroethane and 2-iodopropane for the tungsten analog, and in mixtures of ethyl iodide and 1,2-dibromoethane for $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$. [b] μ = linear absorption coefficient for Mo Kα radiation. [c] n = number of reflections used in calculation of lattice parameters. [d] m = number of reflections with 2θ between 10 and 35° used in least-squares refinement. [e] mt = total number of observed reflections with 2θ 2.5–45°. [f] Unweighted reliability index $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|](100)$. [g] Weighted reliability index $R = [w||F_o| - |F_c||^2/w|F_o|^2]^{1/2}(100)$.

Determination of the Structures. (a) $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$. A three-dimensional Patterson map[41–44] revealed the positions of

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(33) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 216–217.

(34) D. H. Templeton, *Acta Crystallogr.*, 8, 842 (1955).

(35) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, 17, 1040 (1964).

(36) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(37) Reference 33, Vol. I, 1952, p 89.

(38) Reference 37, p 101.

(39) Reference 37, p 74.

(40) Reference 37, p 75.

(41) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965.

(42) The interpretation of the Patterson map in terms of the correct positioning of the tungsten and nickel atoms in the unit cell was checked by the successful application of the computer programs FAME, MAGIC, and LINK[43] based on the Hauptman–Karle centrosymmetric symbolic addition method.[44]

(43) R. B. K. Dewar and A. L. Stone, "Fame and Magic, Fortran Computer Programs for Use in the Symbolic Addition Method," University of Chicago, 1966; *cf.* E. B. Fleischer, R. B. K. Dewar, and A. L.

two tungsten atoms. A structure-factor calculation followed by an electron-density map yielded initial positions of three nickel atoms. However, an electron-density map phased on these five metal atoms gave no information about the other atoms because of many large noise peaks near the positions of the metal atoms. Least-squares refinement[45,46] with anisotropic thermal parameters for both the tungsten and nickel atoms yielded unweighted and weighted discrepancy factors of $R_1 = 28\%$ and $R_2 = 23\%$. A structure-factor calculation followed by a difference Fourier synthesis revealed the positions of the following atoms: (1) two carbonyl groups, the oxygen atom of a third carbonyl group, and the carbon atom of a fourth carbonyl group attached to one tungsten atom; (2) four carbonyl groups attached to the second tungsten atom; (3) a carbonyl group bridging each pair of the three nickel atoms; and (4) the terminal carbonyl group attached to one nickel atom, the oxygen atom of the terminal group for the second nickel atom, and a carbon atom of the terminal carbonyl group attached to the third nickel atom. The positional and anisotropic thermal parameters of the tungsten and nickel atoms were refined by three cycles of least squares without refinement of the atomic parameters of the carbon and oxygen atoms. The subsequent difference Fourier synthesis revealed the positions of carbon and oxygen atoms such that each tungsten atom then had four equatorial carbonyl groups and the nickel triangle had a carbonyl group bridging each edge and one terminal carbonyl group per nickel atom. Two peaks appeared again on this map at the positions corresponding to oxygen atoms of two apical carbonyl groups attached to the two tungsten atoms. However, as before, these two peaks were ignored because no peak was found corresponding to the carbon atom of an apical carbonyl group. Eight peaks, which were presumed to possibly correspond to atomic positions of the two independent $[(C_2H_5)_4N]^+$ cations, were found and included as initial positions of carbon atoms in two subsequent least-squares cycles. One of these atoms was bonded to two others, but the other five were not bonded to or near to each other. The atomic parameters of the metal atoms were least-squares refined as previously stated, and then a cycle of refinement was attempted in which the positional parameters of the carbon and oxygen atoms were varied. Large shifts of the positional parameters of the carbonyl carbon atoms resulted in chemically unreasonable metal–carbon and carbon–oxygen distances. The metal–oxygen distances remained about 3.0 Å for the terminal carbonyl groups and 2.8 Å for the bridging carbonyl groups. Only three of the eight peaks previously assigned as carbon atoms of the cation had shifts of less than 0.2 Å and hence were the only ones retained for the subsequent least-squares cycle.

In order to refine the positional and thermal parameters of the carbonyl groups a noncrystallographic symmetry-constrained least-squares refinement[47] was attempted. The idealized model used for refinement was C_{4v} symmetry for each $W(CO)_4$ fragment and D_{3h} symmetry for the $Ni_3(CO)_6$ fragment. Each $W(CO)_4$ fragment was allowed to rotate about the fourfold axis and the W(1)–W(2)–CO angle was varied but constrained to the C_{4v} model. An isotropic group temperature factor was varied for each $W(CO)_4$ group. The initial distance assumed in this rigid-body model were Ni–CO(terminal) = 1.85 Å, Ni–CO(bridging) = 1.90 Å, W–CO = 1.95 Å, and C–O = 1.15 Å, where the distances were obtained by an averaging of all chemically equivalent bond lengths for the structure. The atomic parameters of the carbonyl groups of the $Ni_3(CO)_6$ fragment were held constant owing to program limitations. Two cycles of least-squares refinement with the above constraints resulted in unrealistically high isotropic group temperature factors of 8 and 17 Å², which is in addition to the fixed values of 5.5 and 6.5 Å² assigned to the carbon and oxygen atoms, respectively. Because the initial set of idealized positions for all the carbonyl groups placed each carbonyl carbon atom within 0.2 Å of its previous position, the idealized coordinates were used in a structure-factor calculation followed by a difference Fourier synthesis. The usual result obtained; the four largest peaks were less than 1.0 Å from the anisotropically least-squares-refined tungsten atoms and had peak heights approximately twice that of other peaks, while the next largest peaks were inside the W_2Ni_3 cluster at chemically unreasonable positions. Only the peaks due to the nickel atoms on the first electron-density map were larger than the noise peaks found on every Fourier map. Peaks on the above Fourier maps were chosen as the positions of atoms on the basis of chemically reasonable distances, because the presumed noise ruled out the possibility that the peaks with the greatest heights corresponded to atoms. The most obvious explanation for not observing peaks for the atoms of the $[(C_2H_5)_4N]^+$ cations is their presumed disorder. Efforts to obtain even the possible orientation of the two independent tetraethylammonium cations from stereochemical considerations of known geometries[48-51] were for naught. It was reluctantly decided to abandon this problem with the hope that the PPN salts of the molybdenum and tungsten compounds would allow a refined solution of the anionic structure. The rationalization for the apparent disorder of the tetraethylammonium cations is that they are not sufficiently large to use with the large $[W_2Ni_3(CO)_{16}]^{2-}$ anion; the considerable dissimilarity in size of these two kinds of ions results in observed close anion···anion contacts such that the much smaller cations may be expected to be loosely packed inside the resulting large cavities created by the $[W_2Ni_3(CO)_{16}]^{2-}$ anions. Since the tetraethylammonium cation possesses an almost spherical van der Waals shape, it can pack with various orientations of its atoms and yet maintain essentially the same intermolecular contacts.[48-51] It was hoped that the highly asymmetrical nature of the much larger PPN cation would lead to an ordered crystal structure for these anions. At this stage of refinement the six W–Ni distances in $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$ were 3.07, 2.99, 3.15, 3.18, 3.08, and 3.13 Å, while the three Ni–Ni distances were 2.37, 2.40, and 2.36 Å. The unweighted and weighted discrepancy factors for 2322 observed reflections were $R_1 = 28\%$ and $R_2 = 21\%$.

(b) $[PPN]_2[W_2Ni_3(CO)_{16}]$ and $[PPN]_2[Mo_2Ni_3(CO)_{16}]$. The compounds $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ and $[PPN]_2[W_2Ni_3(CO)_{16}]$ were then used to solve for the basic structure of the anion. The solutions of the two structures are interrelated and therefore they will be described together with specific differences noted explicitly.

A three-dimensional Patterson map revealed the position of the one crystallographically independent tungsten atom. Structure factors were calculated in the space group $P\bar{1}$ with the center of symmetry midway between the tungsten atoms of the anion. These structure factors were used to phase an electron-density synthesis[41] which revealed the positions of the six half-weighted nickel atoms (disordered owing to the centric nature of the map), four carbonyl groups attached to the tungsten atom, and the phosphorus and nitrogen atom of the cation. The peak heights of the phosphorus and half-weighted nickel atoms were similar, indicating that the two cations are centrosymmetrically related, while the symmetry of the anion was in doubt. One orientation of the nickel triangle along with the centrically related positions for the other known atoms was chosen for an acentric structure factor calculation and subsequent electron-density map corresponding to $P1$ symmetry. Only peaks smaller than that of a carbon atom were found on this map at the sites centrically related to the three nickel atoms. The fifth carbonyl attached to each tungsten atom and all but two phenyl carbon atoms were disclosed on this electron-density map. The phenyl carbon atoms were fitted to an idealized D_{6h} ring with C–C distance of 1.39 Å. In this constrained model each hydrogen atom was required to be 1.08 Å from the carbon atom to which it is bonded and to be collinear with that carbon atom and the midpoint of the phenyl ring. The resulting idealized coordinates for all 12 phenyl groups were used for the next electron-density map. This procedure for the phenyl groups was repeated after each electron density synthesis. With tentative positions defined for all atoms except the carbonyl groups on the trinickel framework, a structure factor calculation followed by a difference Fourier syn-

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Stone, Abstracts, Winter Meeting of the American Crystallographic Association, Atlanta, Ga., 1967, p 20.

(44) (a) H. Hauptman and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," American Crystallographic Association Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa., 1953; (b) *cf.* I. L. Karle and J. Karle, *Acta Crystallogr.*, 16, 969 (1963).

(45) ORFLSD, a local modification of the program by W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(46) Least-squares refinement[45] was based on the minimization of $\Sigma w_i \Delta F_i^2$, and the weights were assigned according to the estimated standard deviations[28] of the observed structure factors. The unweighted and weighted discrepancy factors used are $R_1 = [\Sigma||F_o| - |F_c||/|F_o|]\cdot(100)$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}(100)$.

(47) C. E. Strouse, "Noncrystallographic Symmetry Constraints in Least-Squares Refinements," Ph.D. Thesis (Appendix II), University of Wisconsin, 1969; *Acta Crystallogr., Sect. A*, **26**, 604 (1970).

(48) N. C. Stephenson, *ibid.*, 17, 587 (1964).

(49) G. D. Stucky, J. B. Folkers, and T J. Kistenmacher, *ibid.*, 23, 1064 (1967).

(50) T. Migchelsen and A. Vos, *ibid.*, 23, 796 (1967).

(51) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 7312 (1970).

thesis based on $P1$ symmetry revealed one of the three bridging carbonyl groups and all three terminal carbonyl groups.

Before the least-squares refinement the positions of the nearly centric PPN cations and $W(CO)_5$ fragments were examined. Operating on the atoms of these groups by a crystallographic center of symmetry placed each atom within 0.2 Å of its pseudocentrosymmetrically related mate. The tungsten, phosphorus, nitrogen, and phenyl carbon atoms attached to the phosphorus atoms were all within 0.1 Å of their respective pseudocentrosymmetric partners. It was thought that a refinement of these parameters in the space group $P1$ would fail owing to high correlation of the centrically related atoms; hence the refinement was tentatively started in the $P\bar{1}$ space group.

The addition of a crystallographic center of symmetry to give $P\bar{1}$ symmetry causes the carbon atoms of the terminal carbonyl groups to overlap extensively with the oxygen atoms of the bridging carbonyls. Subsequent least-squares refinements were based on an assumed superimposed positioning of the half-weighted carbon atom of the terminal carbonyl group attached to each nickel and the half-weighted oxygen atom of the carbonyl group bridging the other two nickel atoms. Each of the three resulting coincident pairs of half-weighted atoms was given a scattering power equivalent to a whole-weighted nitrogen atom. The three nickel atoms, the oxygen atom of the terminal carbonyl group bonded to each nickel atom, and the three bridging carbonyl carbon atoms were each half-weighted. With anisotropic thermal parameters for the tungsten atom, isotropic ones for all other nonconstrained atoms, and the one isotropic group temperature factor for each constrained phenyl ring, several cycles of least squares[45,46] were attempted. For the first two cycles on the tungsten compound the only thermal parameters varied were those of the metal and phosphorus atoms and the isotropic group temperature factors for the phenyl rings. The three carbon atoms of the bridging carbonyl groups moved approximately 0.5–0.6 Å. Removing these carbon atoms produced the result that the Ni-Ni distance increased by 0.07 Å on the subsequent two cycles of refinement. Since a half-weighted carbon atom is only 0.8 Å from a half-weighted nickel atom (due to the disordered model assumed), refinement was continued with the molybdenum analog, where the half-weighted carbon atoms would be a larger fraction of the scattering power of the crystal.

A Wilson plot[52] was generated which provided both an initial scale factor and an overall isotropic temperature factor from which the observed structure amplitudes were placed on an absolute scale, and normalized structure factor magnitudes $|E|$ were determined. The statistical averages involving the $|E|$, given below, were found to correspond to neither $P1$ nor $P\bar{1}$.[53] Because of the indecisive nature

	Experimental	Theoretical[53] Centro-symmetric	Noncentro-symmetric
$\langle\|E\|\rangle$	0.826	0.798	0.886
$\langle\|E\|^2\rangle$	1.000	1.000	1.000
$\langle\|E\|^2 - 1\rangle$	0.893	0.968	0.736

of the above values, together with the reasonable distances resulting from the centric refinement of the PPN cation and $W(CO)_4$ fragment for the tungsten compound, refinement of the entire structure in the $P\bar{1}$ space group was continued. A set of initial positional parameters for the $Ni_3(CO)_6$ fragment was estimated from consideration of the final molecular parameters of the corresponding fragment in $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$. This model used initial positions based on D_{3h} symmetry with a Ni–CO (bridging) distance of 1.90 Å and a C–O bond length of 1.15 Å. Though similar to the positions and distances of the refinement of the tungsten analog, the new refinement of the molybdenum compound succeeded because both the positional and thermal parameters of the bridging carbonyl carbon atoms were held constant during the variation of only the positional and anisotropic thermal parameters of the nickel atoms. The nickel–nickel distances had decreased by 0.08 Å at the end of the two cycles of least-squares refinement. With individual isotropic thermal parameters utilized for the constrained phenyl ring carbon atoms as well as for the phosphorus, nitrogen, and all carbonyl carbon and oxygen atoms, the molybdenum compound was refined for two more cycles with fixed bridging carbonyl carbon atomic positions. An attempt was made at this point to refine the structure in the noncentrosymmetric space group $P1$, but the results were as follows: R_1 increased from 8 to 17%; R_2 increased from 13 to 35%; the diagonal elements of the anisotropic thermal parameters for the whole-weighted nickel atoms doubled; whole-weighted bridging carbonyl carbon atoms each moved 0.7–1.1 Å to positions essentially related centrically to the nickel atoms; and the isotropic thermal parameters of these three bridging carbon atoms sharply decreased to unreasonable values between −2.5 and −7.0 Å^2. These results clearly indicated that too much electron density was placed at the positions of the nickel atoms and too little density at the positions centrically related to them, which is consistent with a centrosymmetrically disordered $Ni_3(CO)_6$ fragment such that the *average* unit cell of the entire crystal structure conforms to centrosymmetric $P\bar{1}$ symmetry. This trial refinement under $P1$ symmetry was done with reflections for which $10° < 2\theta < 30°$, and only the parameters of the $Ni_3(CO)_6$ fragment were varied.

During the next two cycles of refinement under $P\bar{1}$ symmetry, only the carbonyl parameters of the $Ni_3(CO)_6$ framework were held constant. Anisotropic thermal parameters were used for each of the three half-weighted nickel atoms, while individual isotropic ones were utilized for each of the phenyl carbon atoms along with fixed isotropic thermal values of 2.0 Å^2 for each hydrogen atom. At the end of two cycles of full-matrix least squares on 1448 observed reflections with $10° < 2\theta < 30°$, the resulting unweighted and weighted discrepancy factors[46] were $R_1 = 6.7$ and $R_2 = 7.4\%$. A structure factor calculation of all 4235 observed reflections was made with all atoms included except for the carbon and oxygen atoms of the crystal-disordered $Ni_3(CO)_6$ fragment. A difference Fourier map clearly revealed the positions of all of these excluded carbonyl atoms with essentially complete overlap of the peaks for the corresponding pairs of terminal carbon and bridging oxygen half-weighted atoms for the two centrosymmetrically related orientations of the $Mo_2Ni_3(CO)_{16}$ anion. Full-matrix least squares[45] of all positional and thermal parameters with 2240 observed data for which $10° < 2\theta < 35°$ resulted in an $R_1 = 6.0$ and $R_2 = 6.5\%$.

The atomic parameters obtained previously for the $W(CO)_5$ part of the tungsten compound together with the final atomic parameters obtained for the PPN cation and $Ni_3(CO)_6$ fragment of the molybdenum analog were used as initial parameters for the refinement of the tungsten complex. Two cycles of full-matrix least squares[45] of 2375 observed reflections for which $10° < 2\theta < 35°$ resulted in $R_1 = 4.2$ and $R_2 = 5.7\%$. For both compounds all ratios of each parameter shift to its estimated standard deviation were less than 0.75 on the last cycle, with only six of the 207 ratios being between 0.50 and 0.75. The resulting atomic parameters from the output of the last least-squares cycle of both compounds are found in Table II.[54] Interatomic distances and bond angles with estimated standard deviations (which include the effect on the estimated errors in lattice parameters) as calculated with the Busing–Martin–Levy function and error program[55] are given in Table III. Equations of least-squares planes determined by a least-squares method[56] along with distances of atoms from these planes, and angles between the normals of these planes are given in Table IV.

Discussion

Description of the Structure and Consequences of Crystal Disorder. The crystal structure of $[PPN]_2[M_2Ni_3(CO)_{16}]$ (M = Mo, W) consists of discrete $\{[(C_6H_5)_3P]_2N\}^+$ cations and $[M_2Ni_3(CO)_{16}]^{2-}$ anions. The configuration (Figure 1) of the $[M_2Ni_3(CO)_{16}]^{2-}$ anion may be described as a trigonal-bipyramidal cluster of transition metal atoms in which a planar $Ni_3(CO)_6$ fragment of D_{3h}-$\bar{6}2m$ symmetry is symmetri-

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(52) M. J. Buerger, "Crystal Structure Analysis," Wiley, New York, N. Y., 1960, p 234.

(53) (a) *Cf.* G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 321; (b) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).

(54) The observed and calculated structure factors (in electrons) for the $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ and $[PPN]_2[W_2Ni_3(CO)_{16}]$ compounds are deposited as Document No. NAPS-01332 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $5.00 for microfiche or $2.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

(55) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306 Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(56) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.

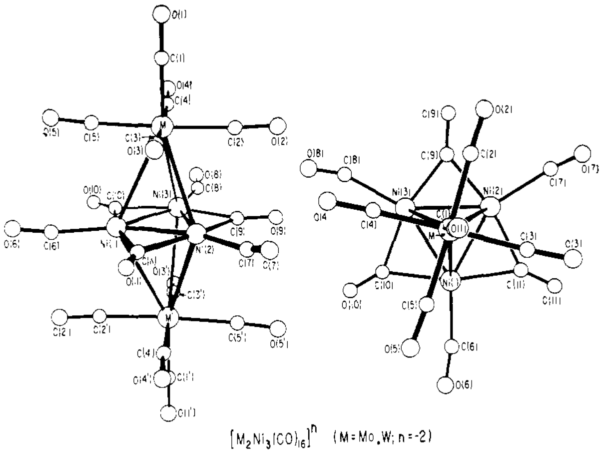

Figure 1. Architecture of the $[M_2Ni_3(CO)_{16}]^n$ anion (M = Cr, Mo, W; $n = -2$). This trigonal-bipyramidal cluster of metal atoms is comprised of a planar $Ni_3(CO)_6$ fragment of idealized D_{3h}-$\bar{6}2m$ geometry which is coordinated by Ni–M interactions to two identical apical $M(CO)_5$ groups, each of idealized C_{4v}-$4mm$ geometry. The resulting idealized geometry of the anion possesses C_{2v}-$2mm$ symmetry with one vertical mirror plane containing the planar $Ni_3(CO)_6$ fragment and the other vertical mirror plane passing through both M atoms, Ni(2), and the midpoint of Ni(1) and Ni(3).

cally coordinated by only Ni–Mo (or Ni–W) interactions to two identical apical $Mo(CO)_5$ (or $W(CO)_5$) groups each of localized C_{4v}-$4mm$ site symmetry. With the assumption of a *regular* D_{3h} trigonal-bipyramidal array of metal atoms, the entire anion approximately possesses a C_{2v}-$2mm$ geometry, with one vertical mirror plane comprising the planar $Ni_3(CO)_6$ fragment (Table IV.A.1) and the other vertical mirror plane passing through both molybdenum (or tungsten) atoms, Ni(2), the midpoint of Ni(1) and Ni(3), C(7), O(7), C(10), and O(10). The twofold axis, which lies along the line of intersection of the two vertical mirror planes, passes through Ni(2), C(7), O(7), C(10), and O(10) (Table IV.A.3). This C_{2v} symmetry is clearly revealed in the projection down the apical M–M′ line (Figure 1); only the top half of the anion is shown in this projection, since the centrosymmetrically related $M'(CO)_5$ fragment essentially superimposes on the $M(CO)_5$ fragment. However, in both the refined $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ and $[PPN]_2[W_2Ni_3(CO)_{16}]$ structures the three Ni–M distances from the $Ni_3(CO)_6$ residue to the one $M(CO)_5$ group are 0.1 Å smaller than the three Ni–M distances from the central $Ni_3(CO)_6$ residue to the other centrosymmetrically related $M(CO)_5$ groups (Table IIIA); the average values are 3.050 *vs.* 3.151 Å in the molybdenum compound and 3.061 *vs.* 3.154 Å in the tungsten compound. This significant difference in metal–metal bond lengths which reduces the idealized geometry of the M_2Ni_3 fragment from D_{3h} to C_{3v}-$3m$ and that of the entire anion from C_{2v} to C_s-m (with the retained mirror plane passing through the two apical M atoms and Ni(2)) may be a consequence of the electronic configuration of the anion (*vide infra*).

The crystal disorder necessarily requires the $Ni_3(CO)_6$ fragment in each anion to appear as two crystallographically related orientations of half-weighted atoms about an average crystallographic symmetry center such that the six half-weighted nickel atoms form a six-pronged star. This "Star of David" disordered arrangement about the centrosymmetric origin in the triclinic unit cell is viewed normal to the $Ni_3(CO)_6$ plane in Figure 2. It is noteworthy that a similar "Star of David" centrosymmetric-disordered arrangement was found to occur in the crystal structure of $Fe_3(CO)_{12}$ for the two isosceles triangles of six half-weighted iron atoms.[57]

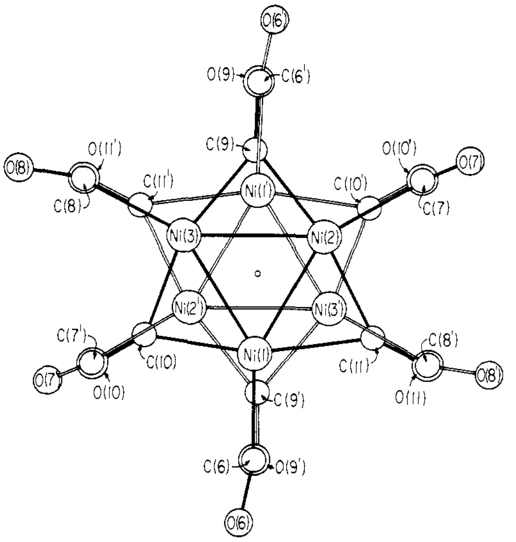

Figure 2. The $Ni_3(CO)_6$ fragment of $\{[(C_6H_5)_3P]_2N\}_2[M_2Ni_3(CO)_{16}]$ (M = Mo, W) in its two statistical orientations about a crystal-averaged center of symmetry.

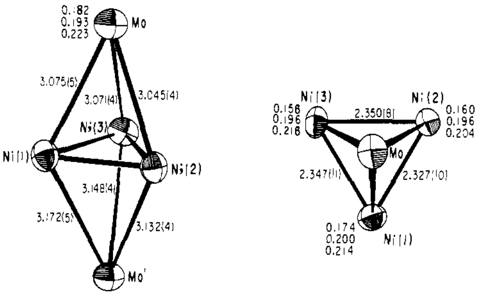

Figure 3. The 50% probability thermal ellipsoids for the Mo_2Ni_3 cluster of $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$. The three root-mean-square components of thermal displacement are given beside each ellipsoid.

Figure 3 gives the 50% probability ellipsoids for the metal atoms in the dimolybdenum–trinickel cluster obtained from the final anisotropic least-squares refinement of these atoms in $[PPN]_2[Mo_2Ni_3(CO)_{16}]$ based on a half-weighting for the disordered nickel atoms and a whole weighting for the crystallographically independent molybdenum atom. The reasonable shapes of the thermal ellipsoids (as reflected by the root-mean-square displacements along the three principal ellipsoidal directions) are in complete accord with the successfully refined crystal-disordered model of $P\bar{1}$ space group symmetry, which assumes a random distribution of each $Ni_3(CO)_6$ fragment in one of two orientations related to each other by a crystallographic center of symmetry such that on the average one-half of each atom in this fragment occupies each atomic site with complete superposition of the corresponding half-weighted terminal carbonyl carbon and half-weighted

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(57) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

Table II. Atomic Parameters for (a) $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$ and (b) $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$

Atom		A. Positional and Isothermal Parameters[a]			
		x	*y*	*z*	*B*, Å²
Mo	(a)	0.98740 (8)	0.14135 (7)	0.17184 (9)	*b*
W	(b)	0.98721 (4)	0.14119 (4)	0.17091 (5)	*b*
Ni(1)	(a)	0.9868 (5)	0.0686 (4)	−0.0926 (6)	*b*
	(b)	0.9860 (5)	0.0692 (5)	−0.0931 (7)	*b*
Ni(2)	(a)	0.9129 (5)	0.0025 (5)	0.0207 (7)	*b*
	(b)	0.9140 (6)	0.0029 (5)	0.0211 (7)	*b*
Ni(3)	(a)	1.1037 (5)	−0.0593 (5)	0.0734 (7)	*b*
	(b)	1.1028 (6)	−0.0583 (6)	0.0734 (8)	*b*
C(1)	(a)	0.9705 (9)	0.2392 (9)	0.2875 (11)	4.9 (3)
	(b)	0.9728 (11)	0.2385 (11)	0.2904 (14)	5.4 (3)
O(1)	(a)	0.9591 (6)	0.2992 (6)	0.3585 (8)	5.7 (2)
	(b)	0.9604 (8)	0.2985 (7)	0.3606 (9)	5.9 (2)
C(2)	(a)	0.9594 (9)	0.0640 (9)	0.2890 (12)	4.8 (3)
	(b)	0.9605 (11)	0.0637 (10)	0.2894 (13)	4.7 (3)
O(2)	(a)	0.9410 (7)	0.0238 (6)	0.3611 (8)	6.3 (2)
	(b)	0.9414 (8)	0.0240 (7)	0.3602 (10)	6.4 (2)
C(3)	(a)	0.8246 (11)	0.2207 (9)	0.0951 (11)	4.9 (3)
	(b)	0.8270 (12)	0.2186 (10)	0.0949 (12)	4.5 (3)
O(3)	(a)	0.7302 (7)	0.2714 (6)	0.0636 (8)	6.0 (2)
	(b)	0.7332 (9)	0.2699 (8)	0.0631 (9)	6.2 (2)
C(4)	(a)	1.1483 (11)	0.0728 (9)	0.2602 (12)	5.3 (3)
	(b)	1.1474 (14)	0.0714 (12)	0.2564 (15)	6.0 (4)
O(4)	(a)	1.2410 (8)	0.0407 (6)	0.3141 (8)	7.0 (2)
	(b)	1.2396 (10)	0.0398 (8)	0.3118 (10)	7.3 (3)
C(5)	(a)	1.0207 (10)	0.2186 (9)	0.0638 (11)	5.0 (3)
	(b)	1.0204 (11)	0.2150 (10)	0.0608 (13)	4.8 (3)
O(5)	(a)	1.0450 (7)	0.2632 (6)	0.0057 (8)	6.4 (8)
	(b)	1.0429 (8)	0.2637 (8)	0.0029 (9)	6.5 (2)
C(6), O(9′)	(a)	0.9710 (7)	0.1554 (10)	−0.2167 (13)	4.4 (2)
	(b)	0.9718 (9)	0.1531 (11)	−0.2169 (13)	5.0 (3)
C(7), O(10′)	(a)	0.7872 (17)	0.0016 (9)	0.0546 (12)	6.9 (3)
	(b)	0.7940 (18)	0.0008 (9)	0.0540 (12)	6.1 (3)
C(8), O(11′)	(a)	1.2473 (17)	−0.1486 (10)	0.1766 (13)	5.9 (3)
	(b)	1.2419 (19)	−0.1444 (12)	0.1736 (15)	6.3 (3)
O(6)	(a)	0.9762 (13)	0.2055 (14)	−0.2763 (17)	5.5 (4)
	(b)	0.9789 (15)	0.2029 (15)	−0.2774 (19)	5.8 (4)
O(7)	(a)	0.7207 (22)	0.0194 (15)	0.0768 (20)	8.7 (7)
	(b)	0.7254 (24)	0.0132 (17)	0.0779 (22)	7.8 (6)
O(8)	(a)	1.3290 (21)	−0.1777 (14)	0.2187 (19)	7.5 (5)
	(b)	1.3254 (24)	−0.1758 (17)	0.2171 (22)	7.6 (6)
C(9)	(a)	1.0224 (28)	−0.1011 (27)	0.1419 (35)	1.8 (10)
	(b)	1.1083 (41)	−0.0930 (35)	0.1406 (41)	2.3 (15)
C(10)	(a)	1.1431 (53)	0.0020 (22)	−0.0364 (32)	3.8 (11)
	(b)	1.1317 (40)	0.0029 (23)	−0.0325 (32)	1.3 (12)
C(11)	(a)	0.8312 (48)	0.1046 (35)	−0.1226 (44)	5.3 (12)
	(b)	0.8395 (53)	0.0971 (42)	−0.1125 (54)	4.8 (17)
P(1)	(a)	0.3105 (2)	0.3140 (2)	0.5063 (3)	*b*
	(b)	0.3100 (3)	0.3141 (2)	0.5046 (3)	*b*
N	(a)	0.4094 (7)	0.2696 (6)	0.4474 (8)	3.5 (2)
	(b)	0.4072 (8)	0.2707 (7)	0.4447 (9)	3.4 (2)
P(2)	(a)	0.4422 (2)	0.3004 (2)	0.3347 (3)	*b*
	(b)	0.4424 (3)	0.3001 (2)	0.3345 (3)	*b*
			$C_6H_5(1)$		
PC(1–1)	(a)	0.1837	0.4035	0.4025	3.7 (3)
	(b)	0.1840	0.4026	0.4007	3.3 (3)
PC(1–2)	(a)	0.1493	0.5044	0.4096	4.7 (3)
	(b)	0.1483	0.5032	0.4087	4.3 (3)
PC(1–3)	(a)	0.0580	0.5735	0.3175	6.0 (3)
	(b)	0.0567	0.5716	0.3174	5.8 (4)
PC(1–4)	(a)	0.0012	0.5417	0.2181	5.5 (3)
	(b)	0.0009	0.5395	0.2182	5.8 (3)
PC(1–5)	(a)	0.0357	0.4408	0.2110	6.4 (3)
	(b)	0.0367	0.4389	0.2103	6.0 (4)
PC(1–6)	(a)	0.1269	0.3717	0.3031	4.7 (3)
	(b)	0.1282	0.3704	0.3015	5.0 (3)
PH(1–2)	(a)	0.1934	0.5291	0.4866	2.0
	(b)	0.1916	0.5281	0.4856	2.0
PH(1–3)	(a)	0.0313	0.6518	0.3230	2.0
	(b)	0.0290	0.6497	0.3235	2.0
PH(1–4)	(a)	−0.0696	0.5953	0.1466	2.0
	(b)	−0.0701	0.5926	0.1475	2.0
PH(1–5)	(a)	−0.0084	0.4161	0.1340	2.0
	(b)	−0.0066	0.4140	0.1334	2.0
PH(1–6)	(a)	0.1536	0.2934	0.2976	2.0
	(b)	0.1560	0.2924	0.2954	2.0

Table II (*Continued*)

Atom		*x*	*y*	*z*	*B*, Å^2
$C_6H_5(2)$					
PC(2–1)	(a)	0.2947	0.2129	0.5551	4.1 (3)
	(b)	0.2944	0.2123	0.5554	4.3 (3)
PC(2–2)	(a)	0.1957	0.2276	0.5713	5.9 (3)
	(b)	0.1961	0.2262	0.5723	5.8 (3)
PC(2-3)	(a)	0.1867	0.1484	0.6177	7.4 (4)
	(b)	0.1880	0.1469	0.6184	7.5 (4)
PC(2–4)	(a)	0.2768	0.0546	0.6478	6.3 (3)
	(b)	0.2782	0.0537	0.6476	6.8 (4)
PC(2–5)	(a)	0.3759	0.0399	0.6315	6.6 (3)
	(b)	0.3765	0.0398	0.6307	7.0 (4)
PC(2–6)	(a)	0.3849	0.1191	0.5851	5.7 (3)
	(b)	0.3846	0.1191	0.5846	5.6 (3)
PH(2–2)	(a)	0.1258	0.3003	0.5480	2.0
	(b)	0.1261	0.2984	0.5497	2.0
PH(2–3)	(a)	0.1098	0.1597	0.6303	2.0
	(b)	0.1118	0.1576	0.6315	2.0
PH(2–4)	(a)	0.2698	−0.0068	0.6837	2.0
	(b)	0.2720	−0.0078	0.6833	2.0
PH(2–5)	(a)	0.4457	−0.0328	0.6548	2.0
	(b)	0.4465	−0.0324	0.6533	2.0
PH(2–6)	(a)	0.4617	0.1078	0.5725	2.0
	(b)	0.4608	0.1084	0.5715	2.0
$C_6H_5(3)$					
PC(3–1)	(a)	0.3397	0.3699	0.6458	3.9 (3)
	(b)	0.3395	0.3706	0.6564	4.1 (3)
PC(3–2)	(a)	0.4458	0.3567	0.6984	4.4 (3)
	(b)	0.4454	0.3565	0.6994	4.7 (3)
PC(3–3)	(a)	0.4710	0.3976	0.8098	6.0 (3)
	(b)	0.4699	0.3977	0.8102	6.1 (4)
PC(3–4)	(a)	0.3901	0.4517	0.8683	6.3 (3)
	(b)	0.3885	0.4529	0.8673	6.2 (4)
PC(3–5)	(a)	0.2841	0.4649	0.8161	6.9 (4)
	(b)	0.2826	0.4670	0.8135	7.5 (4)
PC(3–6)	(a)	0.2589	0.4240	0.7046	5.5 (3)
	(b)	0.2582	0.4259	0.7026	6.2 (4)
PH(3–2)	(a)	0.5085	0.3148	0.6527	2.0
	(b)	0.5085	0.3137	0.6551	2.0
PH(3–3)	(a)	0.5532	0.3874	0.8506	2.0
	(b)	0.5520	0.3868	0.8520	2.0
PH(3–4)	(a)	0.4097	0.4834	0.9551	2.0
	(b)	0.4075	0.4848	0.9533	2.0
PH(3–5)	(a)	0.2214	0.5068	0.8617	2.0
	(b)	0.2196	0.5098	0.8577	2.0
PH(3-6)	(a)	0.1766	0.4342	0.6639	2.0
	(b)	0.1761	0.4368	0.6609	2.0
$C_6H_5(4)$					
PC(4–1)	(a)	0.5818	0.2735	0.3890	3.0 (2)
	(b)	0.5815	0.2735	0.3879	2.8 (2)
PC(4–2)	(a)	0.6550	0.1926	0.4795	3.6 (2)
	(b)	0.6536	0.1928	0.4779	3.5 (3)
PC(4–3)	(a)	0.7656	0.1682	0.5195	4.2 (3)
	(b)	0.7641	0.1675	0.5177	4.2 (3)
PC(4–4)	(a)	0.8030	0.2247	0.4690	4.5 (3)
	(b)	0.8023	0.2228	0.4675	5.0 (3)
PC(4–5)	(a)	0.7299	0.3056	0.3785	5.0 (3)
	(b)	0.7302	0.3035	0.3775	4.3 (3)
PC(4–6)	(a)	0.6193	0.3300	0.3385	4.0 (3)
	(b)	0.6197	0.3288	0.3377	4.2 (3)
PH(4–2)	(a)	0.6259	0.1488	0.5187	2.0
	(b)	0.6239	0.1499	0.5168	2.0
PH(4–3)	(a)	0.8223	0.1055	0.5897	2.0
	(b)	0.8200	0.1050	0.5874	2.0
PH(4–4)	(a)	0.8888	0.2058	0.5001	2.0
	(b)	0.8880	0.2032	0.4983	2.0
PH(4–5)	(a)	0.7590	0.3494	0.3394	2.0
	(b)	0.7599	0.3464	0.3386	2.0
PH(4–6)	(a)	0.5626	0.3927	0.2683	2.0
	(b)	0.5638	0.3913	0.2680	2.0
$C_6H_5(5)$					
PC(5–1)	(a)	0.3662	0.4284	0.2779	3.0 (2)
	(b)	0.3658	0.4279	0.2773	3.3 (3)
PC(5–2)	(a)	0.3808	0.4962	0.3584	3.6 (2)
	(b)	0.3808	0.4953	0.3577	3.8 (3)
PC(5–3)	(a)	0.3197	0.5974	0.3190	4.2 (3)
	(b)	0.3207	0.5960	0.3184	4.2 (3)

Table II (*Continued*)

Atom		*x*	*y*	*z*	*B*, Å^2
PC(5–4)	(a)	0.2439	0.6308	0.1990	4.7 (3)
	(b)	0.2457	0.6295	0.1987	4.8 (3)
PC(5–5)	(a)	0.2293	0.5630	0.1184	5.2 (3)
	(b)	0.2307	0.5621	0.1184	5.5 (3)
PC(5–6)	(a)	0.2905	0.4618	0.1579	4.2 (3)
	(b)	0.2908	0.4613	0.1577	4.6 (3)
PH(5–2)	(a)	0.4395	0.4703	0.4515	2.0
	(b)	0.4389	0.4693	0.4504	2.0
PH(5–3)	(a)	0.3309	0.6500	0.3814	2.0
	(b)	0.3322	0.6483	0.3806	2.0
PH(5–4)	(a)	0.1965	0.7093	0.1684	2.0
	(b)	0.1991	0.7076	0.1683	2.0
PH(5–5)	(a)	0.1706	0.5889	0.2054	2.0
	(b)	0.1726	0.5880	0.0257	2.0
PH(5–6)	(a)	0.2792	0.4092	0.0954	2.0
	(b)	0.2792	0.4091	0.0954	2.0
			C$_6$H$_5$(6)		
PC(6–1)	(a)	0.4290	0.2331	0.2060	4.3 (3)
	(b)	0.4288	0.2325	0.2037	4.3 (3)
PC(6–2)	(a)	0.3613	0.1885	0.1926	7.5 (4)
	(b)	0.3613	0.1883	0.1908	7.9 (4)
PC(6–3)	(a)	0.3457	0.1388	0.0868	11.0 (5)
	(b)	0.3446	0.1395	0.0849	10.8 (6)
PC(6–4)	(a)	0.3978	0.1337	−0.0058	9.3 (4)
	(b)	0.3955	0.1350	−0.0081	9.5 (5)
PC(6–5)	(a)	0.4655	0.1783	0.0076	8.2 (4)
	(b)	0.4630	0.1792	0.0047	8.9 (5)
PC(6–6)	(a)	0.4811	0.2280	0.1135	6.5 (3)
	(b)	0.4797	0.2280	0.1107	6.2 (4)
PH(6–2)	(a)	0.3210	0.1925	0.2644	2.0
	(b)	0.3219	0.1918	0.2630	2.0
PH(6–3)	(a)	0.2932	0.1042	0.0764	2.0
	(b)	0.2922	0.1052	0.0749	2.0
PH(6–4)	(a)	0.3857	0.0952	−0.0879	2.0
	(b)	0.3825	0.0972	−0.0903	2.0
PH(6–5)	(a)	0.5059	0.1744	−0.0642	2.0
	(b)	0.5024	0.1757	−0.0674	2.0
PH(6–6)	(a)	0.5336	0.2626	0.1238	2.0
	(b)	0.5320	0.2623	0.1207	2.0

B. Rigid Body Parameters[c]

Group		*x*	*y*	*z*
C$_6$H$_5$(1)	(a)	0.1837 (5)	0.4035 (5)	0.4025 (6)
	(b)	0.1840 (6)	0.4026 (6)	0.4007 (7)
C$_6$H$_5$(2)	(a)	0.2948 (7)	0.2129 (5)	0.5551 (7)
	(b)	0.2944 (8)	0.2123 (6)	0.5554 (8)
C$_6$H$_5$(3)	(a)	0.3397 (5)	0.3699 (5)	0.6458 (6)
	(b)	0.3395 (7)	0.3706 (6)	0.6456 (7)
C$_6$H$_5$(4)	(a)	0.5818 (4)	0.2734 (5)	0.3890 (7)
	(b)	0.5815 (5)	0.2735 (6)	0.3879 (7)
C$_6$H$_5$(5)	(a)	0.3662 (5)	0.4284 (4)	0.2779 (7)
	(b)	0.3658 (6)	0.4279 (4)	0.2773 (8)
C$_6$H$_5$(6)	(a)	0.4290 (7)	0.2331 (5)	0.2060 (7)
	(b)	0.4288 (8)	0.2325 (7)	0.2037 (8)
		ϕ	θ	ρ
C$_6$H$_5$(1)	(a)	154.2 (3)	152.4 (2)	128.3 (3)
	(b)	155.1 (3)	152.0 (3)	128.5 (3)
C$_6$H$_5$(2)	(a)	−127.2 (2)	−176.5 (3)	−159.5 (3)
	(b)	−126.9 (3)	−176.9 (3)	−159.5 (3)
C$_6$H$_5$(3)	(a)	67.6 (2)	−178.4 (2)	−122.7 (2)
	(b)	66.8 (3)	−179.2 (3)	−122.8 (3)
C$_6$H$_5$(4)	(a)	−26.6 (3)	142.1 (2)	157.5 (3)
	(b)	−27.3 (3)	142.2 (3)	157.6 (5)
C$_6$H$_5$(5)	(a)	126.6 (5)	119.1 (2)	142.3 (5)
	(b)	126.3 (5)	118.9 (3)	142.0 (5)
C$_6$H$_5$(6)	(a)	−78.7 (3)	159.8 (3)	121.7 (3)
	(b)	−78.5 (4)	159.5 (3)	121.0 (4)

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[a] Estimated standard deviations of last significant figures are given in parentheses. [b] Anisotropic thermal parameters of the form exp$[-(\beta_{11}h^2 + \beta_{12}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were used for the metal and phosphorus atoms. The resulting thermal coefficients ($\times 10^4$) are listed below.

Atom		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	(a)	45.4 (10)	47.7 (8)	76.4 (14)	−21.8 (7)	19.2 (9)	−14.4 (7)
W	(b)	55.4 (7)	45.8 (6)	78.4 (9)	−20.4 (4)	22.5 (5)	−14.6 (4)

Table II (*Continued*)

Atom		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	(a)	53 (6)	37 (4)	68 (6)	−16 (5)	16 (6)	2 (4)
	(b)	53 (6)	39 (5)	67 (7)	−13 (5)	19 (7)	−2 (5)
Ni(2)	(a)	39 (7)	42 (4)	70 (7)	−17 (4)	21 (5)	−5 (4)
	(b)	48 (7)	43 (4)	83 (8)	−22 (5)	30 (6)	−12 (4)
Ni(3)	(a)	33 (5)	46 (3)	71 (7)	−15 (3)	15 (5)	−9 (5)
	(b)	40 (8)	43 (4)	77 (9)	−15 (4)	21 (6)	−13 (5)
P(1)	(a)	48 (3)	48 (2)	90 (4)	−26 (2)	28 (3)	−11 (2)
	(b)	53 (3)	43 (3)	90 (4)	−24 (2)	29 (3)	−9 (3)
P(2)	(a)	41 (3)	40 (2)	73 (4)	−18 (2)	16 (3)	−11 (2)
	(b)	48 (3)	33 (2)	66 (4)	−16 (2)	21 (3)	−11 (2)

[c] The three angles ϕ, θ, ρ represent the series of Eulerian rotations which bring an orthonormal basis set of vectors (x, y, z) into coincidence with a second orthonormal set (x''', y''', z'''). The starting set (x, y, z) is defined according to: x along a of the crystallographic basis set, z along $a \times b$, and y along $z \times x$; this places b in the xy plane. The series of Eulerian rotations which take x, y, z into x''', y''', z''' are: ϕ about z to form (x', y', z'); θ about x' to form (x'', y'', z''); finally ρ about y'' to form (x''', y''', z'''), all rotations counterclockwise. A carbon–carbon bond length of 1.392 Å, a carbon–hydrogen bond length of 1.08 Å, and D_{6h} symmetry were assumed for each group.

bridging carbonyl oxygen atoms for the two orientations.

The configuration of the remarkably crystal-stabilizing bis(triphenylphosphine)iminium cation, which has two triphenylphosphine ligands coordinated to a central nitrogen atom (additionally possessing two unshared electron pairs), is presented in Figure 4. The approximate C_2-2 conformation of this PPN cation as well as the observed average P–N bond lengths and P–N–P bond angle in the molybdenum compound (1.578 (6) Å and 137.5 (5)°) and the tungsten analog (1.572 (7) Å and 139.0 (7)°) compare closely with the corresponding values in three previous determinations of its structure in $[PPN]_2[M_2(CO)_{10}] \cdot CH_2Cl_2$ (M = Cr, Mo)[51] and in $[PPN][Cr_2(CO)_{10}I]$.[58] Its stereochemistry and chemical implications are discussed in detail elsewhere.[58]

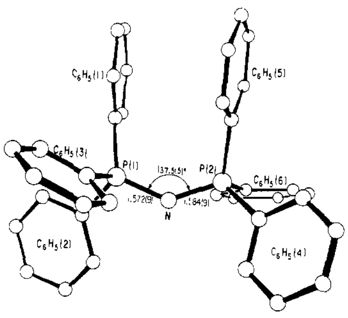

Figure 4. Bis(triphenylphosphine)iminum cation, $\{[(C_6H_5)_3P]_2N\}^+$, which has idealized C_2-2 geometry.

Figure 5 shows the [001] projection of the centrosymmetric triclinic $[PPN]_2[M_2Ni_3(CO)_{16}]$ unit cell containing one anion with its centroid located at the origin and two $\{[(C_6H_5)_3P]_2N\}^+$ cations centrosymmetrically related to each other. For the purposes of clarity, only one orientation of the anion is shown. In the crystal structure of the molybdenum and tungsten compounds the carbonyl oxygen atoms of the $[M_2Ni_3(CO)_{16}]^{2-}$ anion make a large number of contacts (Table IIID) of range 3.0–3.4 Å with the phenyl carbon atoms of the cation, but only one close contact (Table IIID) of 3.0 Å with a carbonyl oxygen atom of another $[M_2Ni_3(CO)_{16}]^{2-}$ anion; the shortest oxygen(anion)···hydrogen(cation) contacts are greater than 2.4 Å except for one closer distance of 2.2 Å between a phenyl hydrogen atom and a bridging carbonyl oxygen atom. These above reasonable distances which are all compatible with corresponding distances in structures of other metal carbonyl complexes do not indicate any unusual interactions except possibly a weak hydrogon bonding of the particular phenyl carbon hydrogen atom cited above with the bridging carbonyl oxygen atom which is expected to be more electronegative than the terminal oxygen ones.

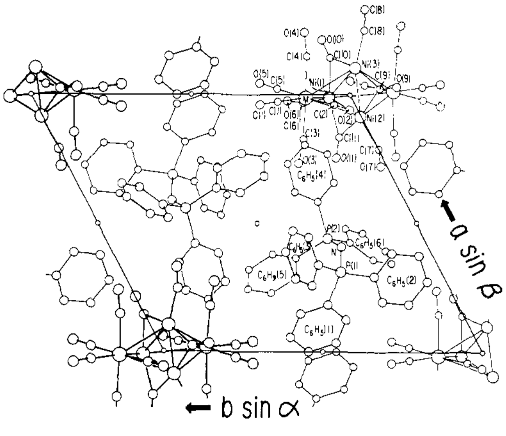

Figure 5. [001] projection of the centrosymmetric triclinic unit cell of $\{[(C_6H_5)_3P]_2N\}_2[M_2Ni_3(CO)_{16}]$. Only one orientation of the disordered $Ni_3(CO)_6$ fragment per anion is shown.

The corresponding bond lengths and angles (Table III) for the $[Mo_2Ni_3(CO)_{16}]^{2-}$ and $[W_2Ni_3(CO)_{16}]^{2-}$ anions agree remarkably well with each other. The closeness of the corresponding averaged molecular parameters corroborates the fact that the covalent radii for the Mo and W atoms must be nearly identical. Relatively larger uncertainties presumably exist in the positional parameters of the $Ni_3(CO)_6$ fragment due to the crystal disorder, and hence the molecular parameters in this part of the anion are less reliable.

The Mo–CO(equatorial) distances of 1.974 to 2.011 Å are in the range found in $Mo(h^5\text{-}C_5H_5)(CO)_2XY$ complexes[59] such as $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$ (1.946–1.969 Å),[60]

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(58) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7327 (1970).

(59) E. Rodulfo de Gil and L. F. Dahl, *ibid.*, **91**, 3751 (1969).

(60) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27, 809, (1957); F. C. Wilson, Ph.D. Thesis, Massachusetts Institute of Technology, 1957.

Table III. Interatomic Distances and Bond Angles for $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$ and $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$

A. Intramolecular Distances, Å

	M = Mo	M = W
1. Between $M(CO)_5$ and $Ni_3(CO)_6$ Fragment		
M–Ni(1)	3.075 (5)	3.078 (6)
M–Ni(2)	3.045 (5)	3.032 (5)
M–Ni(3)	3.071 (4)	3.062 (5)
	3.064 (av)	3.057 (av)
M′–Ni(1)	3.172 (5)	3.182 (5)
M′–Ni(2)	3.132 (4)	3.136 (5)
M′–Ni(3)	3.148 (4)	3.155 (5)
	3.151 (av)	3.158 (av)
2. $M(CO)_5$ Fragment (Idealized Configuration Has C_{4v}-4*mm* Symmetry)		
M–C(2)	1.996 (13)	2.007 (14)
M–C(3)	2.011 (13)	1.987 (15)
M–C(4)	2.002 (14)	1.997 (17)
M–C(5)	1.974 (14)	1.963 (14)
	1.966 (av)	1.988 (av)
M–C(1)	1.903 (13)	1.935 (16)
C(1)–O(1)	1.166 (12)	1.165 (15)
C(2)–O(2)	1.162 (12)	1.160 (13)
C(3)–O(3)	1.165 (12)	1.165 (14)
C(4)–O(4)	1.164 (12)	1.167 (15)
C(5)–O(5)	1.160 (12)	1.193 (13)
	1.163 (av)	1.171 (av)
3. $Ni_3(CO)_6$ Fragment (Idealized Configuration Has D_{3h}-$\bar{6}2m$ Symmetry)		
Ni(1)–Ni(2)	2.327 (10)	2.324 (12)
Ni(2)–Ni(3)	2.350 (8)	2.334 (9)
Ni(3)–Ni(1)	2.347 (11)	2.360 (12)
	2.341 (av)	2.339 (av)
Ni(1)–C(6)	1.82 (2)	1.81 (2)
Ni(2)–C(7)	1.94 (2)	1.87 (2)
Ni(3)–C(8)	1.91 (2)	1.86 (2)
	1.89 (av)	1.85 (av)
Ni(1)–C(10)	1.91 (5)	1.79 (5)
Ni(1)–C(11)	1.97 (5)	1.90 (6)
Ni(2)–C(9)	1.86 (4)	1.79 (5)
Ni(2)–C(11)	1.94 (5)	1.81 (6)
Ni(3)–C(10)	1.88 (5)	1.76 (5)
Ni(3)–C(9)	1.87 (4)	1.84 (5)
	1.91 (av)	1.82 (av)
C(6)–O(6)	1.06 (2)	1.08 (2)
C(7)–O(7)	0.96 (2)	1.02 (2)
C(8)–O(8)	1.01 (5)	1.04 (2)
	1.01 (av)	1.05 (av)
C(9)–O(9)	1.14 (3)	1.20 (4)
C(10)–O(10)	1.05 (5)	1.13 (4)
C(11)–O(11)	1.02 (5)	1.09 (6)
	1.07 (av)	1.14 (av)
4. $\{[(C_6H_5)_3P]_2N\}$ Cation (Idealized Configuration Has C_2-2 Symmetry)		
P(1)–N	1.572 (9)	1.564 (10)
P(2)–N	1.584 (9)	1.580 (10)
	1.578 (av)	1.572 (av)
P(1)--PC(1–1)	1.783	1.781
P(1)--PC(2–1)	1.770	1.796
P(1)--PC(3–1)	1.774	1.801
P(2)--PC(4–1)	1.773	1.774
P(2)--PC(5–1)	1.774	1.782
P(2)--PC(6–1)	1.742	1.769
	1.769 (av)	1.784 (av)

B. Bond Angles, Deg

	M = Mo	M = W
1. Between $M(CO)_5$ and $Ni_3(CO)_6$ Fragment		
M–Ni–Ni		
M–Ni(1)–Ni(2)	67.0 (2)	66.6 (2)
M–Ni(1)–Ni(3)	67.5 (2)	67.0 (2)
M–Ni(2)–Ni(1)	68.3 (2)	68.7 (2)
M–Ni(2)–Ni(3)	68.0 (2)	68.2 (2)
M–Ni(3)–Ni(2)	66.8 (2)	66.8 (2)
M–Ni(3)–Ni(1)	67.6 (2)	67.8 (2)
	67.5 (av)	67.5 (av)
M′–Ni–Ni		
M′–Ni(1)–Ni(2)	67.4 (2)	67.4 (2)
M′–Ni(1)–Ni(3)	67.7 (2)	67.5 (2)
M′–Ni(2)–Ni(1)	69.3 (2)	69.5 (2)
M′–Ni(2)–Ni(3)	68.4 (2)	68.7 (2)
M′–Ni(3)–Ni(2)	67.7 (2)	67.8 (2)
M′–Ni(3)–Ni(1)	68.7 (2)	68.8 (2)
	68.2 (av)	68.3 (av)
Ni–M–Ni		
Ni(1)–M–Ni(2)	44.7 (2)	44.7 (2)
Ni(1)–M–Ni(3)	44.9 (2)	45.2 (2)
Ni(2)–M–Ni(3)	45.2 (1)	45.0 (2)
	44.9 (av)	45.0 (av)
Ni–M′–Ni		
Ni(1)–M′–Ni(2)	43.3 (2)	43.1 (2)
Ni(1)–M′–Ni(3)	43.6 (2)	43.7 (2)
Ni(2)–M′–Ni(4)	43.9 (1)	43.6 (2)
	43.6 (av)	43.5 (av)
M–Ni–M′		
M–Ni(1)–M′	127.2 (2)	126.7 (3)
M–Ni(2)–M′	129.8 (3)	130.3 (3)
M–Ni(3)–M′	128.2 (2)	128.4 (3)
	128.4 (av)	128.5 (av)
M–Ni–CO (terminal)		
M–Ni(1)–C(6)	116.6 (3)	117.2 (4)
M′–Ni(1)–C(6)	116.6 (3)	116.0 (4)
M–Ni–CO (terminal)		
M–Ni(2)–C(7)	113.9 (4)	114.2 (4)
M′–Ni(2)–C(7)	116.2 (4)	115.5 (5)
M–Ni(3)–C(8)	116.5 (3)	116.3 (4)
M′–Ni(3)–C(8)	115.3 (4)	115.3 (4)
	115.5 (av)	115.3 (av)
M–Ni–CO (bridging)		
M–Ni(1)–C(10)	88.7 (10)	86.5 (11)
M′–Ni(1)–C(10)	84.3 (10)	82.9 (10)
M–Ni(1)–C(11)	88.0 (10)	86.4 (14)
M′–Ni(1)–C(11)	85.1 (10)	83.5 (14)
M–Ni(2)–C(9)	88.0 (9)	86.4 (13)
M′–Ni(2)–C(9)	83.4 (9)	85.2 (13)
M–Ni(2)–C(11)	89.5 (10)	89.4 (13)
M′–Ni(2)-C(11)	86.7 (10)	86.3 (14)
M–Ni(3)–C(9)	87.1 (9)	84.6 (13)
M′–Ni(3)–C(9)	82.9 (9)	83.8 (12)
M–Ni(3)–C(10)	89.3 (10)	87.6 (11)
M′–Ni(3)–C(10)	85.4 (10)	84.3 (10)
	86.5 (av)	85.6 (av)
Ni–M–CO (apical)		
Ni(1)-M–C(1)	153.5 (4)	154.1 (4)
Ni(1)–M′–C(1′)	153.3 (4)	152.5 (4)
Ni(2)–M–C(1)	151.5 (4)	152.1 (4)
Ni(2)–M′–C(1′)	158.3 (4)	158.1 (4)
Ni(3)–M–C(1)	156.2 (4)	155.0 (4)
Ni(3)–M′-C(1′)	151.8 (4)	153.2 (4)
	154.1 (av)	154.2 (av)

Table III (*Continued*)

B. Bond Angles, Deg	M = Mo	M = W
Ni–M–CO (eq)		
Ni(1)–M–C(2)	114.8 (3)	115.2 (4)
Ni(1)–M′–C(5′)	117.6 (4)	116.3 (4)
	116.2 (av)	115.8 (av)
Ni(1)–M–C(5)	67.7 (4)	66.1 (4)
Ni(1)–M′–C(2′)	64.3 (4)	64.3 (4)
	66.0 (av)	65.2 (av)
Ni(1)–M–C(3)	84.9 (3)	84.4 (4)
Ni(1)–M –C(4′)	87.1 (4)	85.9 (4)
	86.0 (av)	85.2 (av)
Ni–M–CO (eq)		
Ni(1)–M–C(4)	100.2 (4)	99.5 (5)
Ni(1)–M –C(3′)	98.2 (3)	98.1 (4)
	99.2 (av)	98.8 (av)
Ni(2)–M–C(2)	71.3 (4)	71.7 (4)
Ni(2)–M′–C(5′)	74.9 (4)	73.8 (4)
	73.1 (av)	72.8 (av)
Ni(2)–M–C(5)	111.5 (4)	110.0 (4)
Ni(2)–M′–C(2′)	106.5 (4)	106.4 (4)
	109.0 (av)	108.2 (av)
Ni(2)–M–C(3)	73.8 (3)	73.6 (4)
Ni(2)–M′–C(4′)	76.3 (4)	75.5 (5)
	75.1 (av)	74.6 (av)
Ni(2)–M–C(4)	111.7 (4)	110.6 (5)
Ni(2)–M′–C(3′)	109.2 (4)	108.7 (4)
	110.5 (av)	109.6 (av)
Ni(3)–M–C(2)	88.4 (4)	84.3 (4)
Ni(3)–M′–C(5′)	89.0 (4)	87.8 (4)
	88.7 (av)	86.0 (av)
Ni(3)–M–C(5)	96.6 (4)	95.3 (4)
Ni(3)–M′–C(2′)	93.8 (4)	94.2 (4)
	95.2 (av)	94.8 (av)
Ni(3)–M–C(3)	117.4 (3)	117.1 (4)
Ni(3)–M′–C(4′)	118.8 (4)	117.7 (5)
	118.1 (av)	117.4 (av)
Ni(3)–M–C(4)	68.3 (4)	67.3 (5)
Ni(3)–M′–C(3′)	66.9 (3)	66.7 (4)
	67.6 (av)	67.0 (av)
2. M(CO)$_5$ Fragment (Idealized Configuration Has C_{4v}-4mm Symmetry)		
M–C–O		
M–C(1)–O(1)	179.3 (10)	177.7 (12)
M–C(2)–O(2)	176.0 (10)	176.0 (12)
M–C(3)–O(3)	172.2 (10)	171.9 (12)
M–C(4)–O(4)	174.3 (11)	172.9 (13)
M–C(5)–O(5)	176.4 (10)	174.3 (12)
	174.7 (av)	173.8 (av)
OC (apical)–M–CO (eq)		
C(1)–M–C(2)	89.4 (5)	88.9 (5)
C(1)–M–C(3)	85.3 (5)	86.7 (6)
C(1)–M–C(4)	89.0 (5)	88.9 (6)
C(1)–M–C(4)	88.5 (5)	90.3 (6)
	88.1 (av)	86.2 (av)
OC (eq)–M–CO (eq)		
C(2)–M–C(3)	88.6 (5)	89.1 (5)
C(2)–M–C(4)	91.6 (5)	91.1 (6)
C(3)–M–C(5)	93.5 (5)	93.5 (5)
C(4)–M–C(5)	86.1 (5)	86.2 (6)
	89.9 (av)	90.0 (av)
OC (eq)–M–CO (eq)		
C(2)–M–C(5)	176.9 (5)	177.2 (5)
C(3)–M–C(4)	174.2 (5)	175.6 (5)
	175.6 (av)	176.4 (av)
3. Ni$_3$(CO)$_6$ Fragment (Idealized Configuration Has D_{3h}-$\bar{6}2m$ Symmetry)		
Ni(1)–Ni(2)–Ni(3)	60.3 (4)	60.9 (4)
Ni(1)–Ni(3)–Ni(2)	59.4 (4)	59.3 (4)
Ni(3)–Ni(1)–Ni(2)	60.4 (3)	59.8 (4)
	60.0 (av)	60.0 (av)
Ni–C(terminal)–O		
Ni(1)–C(6)–O(6)	168.4 (12)	167.8 (14)
Ni(2)–C(7)–O(7)	164.2 (18)	168.5 (18)
Ni(3)–C(8)–O(8)	159.5 (15)	161.0 (18)
	164.0 (av)	165.8 (av)
Ni–C(bridging)–O		
Ni(1)–C(10)–O(10)	143 (3)	139 (3)
Ni(1)–C(11)–O(11)	146 (4)	139 (5)
Ni(2)–C(9)–O(9)	138 (3)	140 (4)
Ni(2)–C(11)–O(11)	141 (3)	143 (4)
Ni(3)–C(9)–O(9)	144 (3)	140 (4)
Ni(3)–C(10)–O(10)	140 (3)	139 (3)
	142 (av)	140 (av)
Ni–C(bridging)–Ni		
Ni(1)–C(11)–Ni(2)	73 (2)	78 (3)
Ni(1)–C(10)–Ni(3)	76 (3)	83 (3)
Ni(2)–C(9)–Ni(3)	78 (2)	80 (2)
	76 (av)	80 (av)
OC(terminal)–M–CO(bridging)		
C(6)–Ni(1)–C(10)	97.4 (16)	100.4 (17)
C(6)–Ni(1)–C(11)	98.2 (16)	102.7 (21)
C(7)–Ni(2)–C(9)	98.4 (15)	97.8 (19)
C(7)–Ni(2)–C(11)	96.5 (14)	97.5 (18)
C(8)–Ni(3)–C(9)	99.1 (15)	101.0 (19)
C(8)–Ni(3)–C(10)	98.5 (14)	101.7 (16)
	98.0 (av)	100.2 (av)
OC(bridging)–Ni–CO(bridging)		
C(10)–Ni(1)–C(11)	163.8 (18)	156.5 (21)
C(9)–Ni(2)–C(11)	164.7 (19)	164.5 (23)
C(9)–Ni(3)–C(10)	161.8 (18)	157.1 (22)
	163.4 (av)	159.4 (av)
C(terminal)–Ni–Ni		
C(6)–Ni(1)–Ni(2)	151.0 (5)	152.1 (6)
C(6)–Ni(1)–Ni(3)	148.6 (5)	148.1 (5)
C(7)–Ni(2)–Ni(1)	150.4 (6)	150.3 (6)
C(7)–Ni(2)–Ni(3)	149.3 (8)	148.7 (8)
C(8)–Ni(3)–Ni(1)	150.7 (6)	150.7 (6)
C(8)–Ni(3)–Ni(2)	149.9 (8)	150.0 (8)
	150.0 (av)	150.0 (av)
C(bridging)–Ni–Ni		
C(9)–Ni(2)–Ni(3)	51.0 (11)	51.0 (11)
C(9)–Ni(3)–Ni(2)	50.8 (11)	48.9 (15)
C(10)–Ni(1)–Ni(3)	51.2 (14)	47.7 (15)
C(10)–Ni(3)–Ni(1)	52.3 (14)	49.0 (15)
C(11)–Ni(1)–Ni(2)	52.8 (14)	49.4 (19)
C(11)–Ni(2)–Ni(1)	54.1 (14)	52.9 (17)
	52.0 (av)	49.8 (av)
C(bridging)–Ni–Ni		
C(9)–Ni(2)–Ni(1)	111.2 (13)	111.9 (17)
C(9)–Ni(3)–Ni(1)	110.2 (13)	108.3 (17)
C(10)–Ni(1)–Ni(2)	111.6 (16)	107.4 (16)
C(10)–Ni(3)–Ni(2)	111.6 (16)	108.3 (17)
C(11)–Ni(1)–Ni(3)	113.2 (15)	109.2 (20)
C(11)–Ni(2)–Ni(3)	114.3 (16)	113.7 (19)
	112.0 (av)	109.8 (av)

Table III (*Continued*)

B. Bond Angles, Deg

	M = Mo	M = W
4. $\{[(C_6H_5)_3P]_2N\}$ Cation (Idealized Configuration Has C_2-2 Symmetry)		
P(1)–N–P(2)	137.5 (5)	139.0 (7)
N–P(1)–PC(1–1)	115.3	114.4
N–P(1)–PC(2–1)	106.7	107.3
N–P(1)–PC(3–1)	111.4	111.7
N–P(2)–PC(4–1)	109.0	110.3
N–P(2)–PC(5–1)	114.2	113.4
N–P(2)–PC(6–1)	111.5	111.5
	111.3 (av)	111.4 (av)
P(1)–PC(1–1)–PC(1–2)	120.5	120.6
P(1)–PC(1–1)–PC(1–6)	118.9	118.9
P(1)–PC(2–1)–PC(2–2)	120.7	121.2
P(1)–PC(2–1)–PC(2–6)	119.2	118.7
P(1)–PC(3–1)–PC(3–2)	119.2	119.4
P(1)–PC(3–1)–PC(3–6)	120.8	120.5
P(2)–PC(4–1)–PC(4–2)	119.3	118.6
P(2)–PC(4–1)–PC(4–6)	120.7	121.3
P(2)–PC(5–1)PC(5–2)	118.3	117.9
P(2)–PC(5–1)–PC(5–6)	121.6	122.1
P(2)–PC(6–1)–PC(6–2)	119.4	119.1
P(2)–PC(6–1)–PC(6–6)	120.5	120.8
	119.9 (av)	119.9 (av)
PC(1–1)–P(1)–PC(2–1)	109.3	109.6
PC(1–1)–P(1)–PC(3–1)	107.4	107.7
PC(2–1)–P(1)–PC(3–1)	106.3	105.7
PC(4–1)–P(2)–PC(5–1)	106.7	106.8
PC(4–1)–P(2)–PC(6–1)	107.1	107.0
PC(5–1)–P(2)–PC(6–1)	108.0	107.5
	107.5 (av)	107.4 (av)

C. Nonbonding Carbon–Carbon Distances

	M = Mo	M = W
1. Between $M(CO)_5$ and $Ni_6(CO)_6$ Fragment		
C(2)···C(7)	3.49 (2)	3.46 (2)
C(2)···C(9)	2.87 (3)	2.79 (4)
C(3)···C(7)	3.61 (2)	3.57 (2)
C(3)···C(11)	2.93 (3)	2.89 (4)
C(4)···C(8)	3.23 (2)	3.16 (2)
C(4)···C(10)	3.39 (4)	3.30 (4)
C(5)···C(6)	3.19 (2)	3.17 (2)
C(5)···C(10)	3.28 (3)	3.18 (3)
2. $M(CO)_5$ Fragment		
C(apical)···C(eq)		
C(1)···C(2)	2.74 (2)	2.76 (2)
C(1)···C(3)	2.65 (2)	2.69 (2)
C(1)···C(4)	2.74 (2)	2.75 (2)
C(1)···C(5)	2.71 (2)	2.76 (2)
C(eq)···C(eq)′		
C(2)···C(3)	2.80 (2)	2.80 (2)
C(2)···C(4)	2.87 (2)	2.86 (2)
C(5)···C(3)	2.90 (2)	2.88 (2)
C(5)···C(4)	2.71 (2)	2.71 (2)
3. $Ni_3(CO)_6$ Fragment		
C(6)···C(10)	2.80 (3)	2.77 (4)
C(6)···C(11)	2.86 (4)	2.89 (5)
C(7)···C(9)	2.88 (4)	2.75 (6)
C(7···C(11)	2.89 (4)	2.76 (5)
C(8)···C(9)	2.88 (4)	2.86 (6)
C(8)···C(10)	2.87 (4)	2.81 (4)

D. Closest Nonbonding Intermolecular Distances

	M = Mo	M = W
1. For Nonhydrogen Atoms		
O(9)···PC(5–4)[a]	3.36	3.42
O(6)···PC(4–4)[b]	3.12	3.16
O(6)···PC(1–3)[a]	3.20	3.27
O(6)···PC(2–3)[c]	3.26	3.24
O(6)···PC(5–4)[a]	3.32	3.40
O(7)···PC(6–5)	3.22	3.33
O(7)···PC(2–4)[g]	3.24	3.24
O(7)···PC(6–4)	3.42	3.39
O(7)···PC(6–3)[d]	3.30	3.26
O(8)···PC(3–2)[f]	3.04	3.09
O(8)···PC(4–2)[f]	3.26	3.30
O(8)···PC(3–3)[f]	3.35	3.40
O(1)···PC(1–6)[h]	3.25	3.28
O(1)···PC(2–2)[h]	3.26	3.26
O(1)···PC(4–5)	3.30	3.23
O(2)···O(2)[f]	2.98	3.02
O(2)···PC(4–4)	3.20	3.19
O(2)···PC(4–3)	3.36	3.37
2. For Nonhydrogen to Hydrogen Atoms		
O(9)···PH(5–4)[a]	2.53	2.59
O(10)···PH(6–3)[d]	2.58	2.63
O(6)···PH(5–4)[a]	2.78	2.87
O(7)···PH(6–3)[d]	2.53	2.49
O(10)···PH(5–4)[e]	2.57	2.60
O(6)···PH(1–3)[a]	2.20	2.27
O(6)···PH(2–3)[c]	2.23	2.22
O(6)···PH(4–4)[b]	2.44	2.46
C(8)···PH(5–4)[a]	2.72	2.83
O(1)···PH(4–5)	2.56	2.57
O(1)···PH(2–2)[h]	2.72	2.71
O(7)···PH(2–4)[g]	2.60	2.62
O(7)···PH(6–4)[d]	2.81	2.79
O(8)···PH(3–2)[f]	2.40	2.43
C(6)···PH(5–4)[e]	2.78	2.93
O(1)···PH(4–4)	2.77	2.89
O(5)···PH(1–5)[h]	2.60	2.59
PC(6–2)···PH(2–5)[a]	2.80	2.92
3. For Hydrogen to Hydrogen Atoms		
PH(1–5)···PH(5–5)[j]	2.54	2.57
PH(3–5)···PH(5–5)[k]	2.25	2.26
PH(5–2)···PH(5–2)[i]	2.31	2.36

[a] $1 - x, 1 - y, z$. [b] $x, y, z - 1$. [c] $1 + x, y, z - 1$. [d] $1 - x, -y, -z$. [e] $1 + x, y - 1, z$. [f] $2 - x, -y, 1 - z$. [g] $1 - x, -y, 1 - z$. [h] $1 + x, y, z$. [i] $1 - x, 1 - y, 1 - z$. [j] $-x, 1 - y; -z$. [k] $x, y, 1 + z$.

Mo(h^5-C_5H_5)$(CO)_3C_3F_7$ (1.990 (9), 1.992 (9), and 2.018 (9) Å),[61] Mo(h^5-C_5H_5)$(CO)_2[P(C_6H_5)_3]COCH_3$ (1.934 (13) and 1.976 (13) Å),[62] and Mo(h^5-C_5H_5)$(CO)_2$(π-CH_2SCH_3) (1.903 (9) and 1.918 (10) Å).[59]

Outline of Bonding Description of $[M_2Ni_3(CO)_{16}]^{2-}$ Anions (M = Cr, Mo, W). In order to gain insight into the nature of the delocalized metal–metal interactions within the $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W), an LCAO-MO model is utilized based primarily on symmetry arguments involving the topological character of the valence wave functions. Although greatly oversimplified, this bonding picture is viewed to be qualitatively valid in accounting for the electronic structure of the anions, including the rationalization of all the experimental data. Similar MO schemes applied to other triangular metal cluster systems have provided experimental predictions which subsequently have been verified.[8,63–66]

The MO model employed here assumes that the $Ni_3(CO)_6$ fragment possesses D_{3h} geometry, while each $M(CO)_5$ fragment has localized C_{4v} site symmetry. Since the geometry of the $Ni_3(CO)_6$ fragment is analogous

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(61) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(62) M. R. Churchill and J. P. Fennessey, *ibid.*, 7, 953 (1968).

(63) F. A. Cotton and T. E. Haas, *ibid.*, 3, 10 (1964).

(64) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 90, 3960 (1968).

(65) H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *ibid.*, 90, 3272 (1968).

(66) C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, 47, 93 (1969).

Table IV. Molecular Planes and Angles between These Planes[a,b] for (a) $\{[(C_6H_5)_3P]_2N\}_2[Mo_2Ni_3(CO)_{16}]$ and (b) $\{[(C_6H_5)_3P]_2N\}_2[W_2Ni_3(CO)_{16}]$

A. Best Molecular Planes and Perpendicular Distances (Å) from These Planes

Atom	M = Mo	M = W	Atom	M = Mo	M = W
1. Plane through Ni(1), Ni(2), Ni(3)					
(a) $-0.1055X - 0.7536Y - 0.6488Z + 1.5580 = 0$					
(b) $-0.1072X - 0.7554Y - 0.6464Z + 1.5947 = 0$					
M	−2.75	−2.74	C(5)	−2.85	−2.80
M′	2.85	2.85	O(5)	−2.95	−2.94
Ni(1′)	0.10	0.11	C(6)	−0.01	0.01
Ni(2′)	0.10	0.11	C(7)	−0.05	−0.03
Ni(3′)	0.10	0.11	C(8)	0.00	−0.00
C(1)	−4.65	−4.68	O(6)	−0.13	−0.11
O(1)	−5.81	−5.84	O(7)	−0.31	−0.24
C(2)	−2.72	−2.72	O(8)	−0.12	−0.10
O(2)	−2.79	−2.77	C(9)	0.08	0.02
C(3)	−2.81	−2.79	C(10)	0.08	0.06
O(3)	−2.99	−2.98	C(11)	0.06	0.06
C(4)	−2.89	−2.85	O(9)	0.11	0.10
O(4)	−3.08	−3.05	O(10)	0.15	0.14
			O(11)	0.10	0.11
2. Least-Squares Plane through C(2), C(3), C(4), C(5)					
(a) $-0.0699X - 0.7491Y - 0.6587Z + 3.8647 = 0$					
(b) $-0.0839X - 0.7532Y - 0.6524Z + 4.0492 = 0$					
C(2)	0.032	0.030	M	0.069	0.046
C(3)	−0.031	−0.030	Ni(1)	2.849	2.809
C(4)	−0.032	−0.031	Ni(2)	2.768	2.757
C(5)	0.032	0.031	Ni(3)	2.835	2.802
O(2)	−0.07	−0.05	C(7)	2.646	2.679
O(3)	−0.24	−0.23	O(7)	2.355	2.448
O(4)	−0.19	−0.22	C(8)	2.860	2.817
O(5)	−0.03	−0.09	O(8)	2.769	2.730
C(1)	−1.83	−1.89	C(9)	2.842	2.776
O(1)	−3.00	−3.05	O(9)	2.847	2.844
C(6)	2.881	2.844	C(10)	2.976	2.898
O(6)	2.794	2.750	O(10)	3.082	3.008
			O(11)	2.868	2.871
3. Plane through M, M′, Ni(2), Ni(2′)					
(a) $-0.0973X + 0.6534Y - 0.7507Z + 1.3922 = 0$					
(b) $-0.0982X + 0.6529Y - 0.7510Z + 1.4105 = 0$					
Ni(1)	1.21	1.23	C(7)	−0.06	−0.08
Ni(3)	−1.13	−1.13	C(10)	0.07	0.06
C(1)	0.03	−0.00	O(7)	0.02	−0.04
O(1)	0.06	0.02	O(10)	0.06	0.08
C(2)	−1.40	−1.42	C(6)	2.80	2.79
C(3)	1.40	1.38	C(8)	−2.77	−2.72
C(4)	−1.39	−1.39	O(6)	3.61	3.61
C(5)	1.32	1.32	O(8)	−3.41	−3.40
O(2)	−2.19	−2.20	C(9)	−1.83	−1.76
O(3)	2.16	2.16	C(11)	1.93	1.80
O(4)	−2.15	−2.16	O(9)	−2.80	−2.79
O(5)	2.05	2.08	O(11)	2.77	2.72

B. Angles (deg) between Normals to Planes

(a)	1–2	2.1	2–3	89.3	3–1	89.7
(b)	1–2	1.4	2–3	89.6	3–1	89.8

[a] The equations of the planes are given in an orthogonal ångström coordinate system (X, Y, Z) which is related to the fractional unit cell coordinate system (x, y, z) as follows: $X = xa + yb \cos\gamma + zc \cos\beta$; $Y = yb \sin\gamma + zc \cos\mu$; $Z = zc \cos\sigma$; where $\cos\mu = (\cos\alpha - \cos\beta \cos\gamma)/\sin\gamma$ and $\sin^2\sigma = 1 - \cos^2\beta - \cos^2\mu$. [b] All atoms were assigned unit weights.

Table V. Representations under D_{3h} Symmetry for the Relevant Symmetry Orbital Combinations of the Three Nickel Atoms and Two Molybdenum Atoms

Three Ni 4s	$a_1' + e'$	Three Ni $3d_{xy}$	$a_1'' + e''$
Three Ni $4p_z$	$a_1' + e'$		
Three Ni $3d_{z^2}$	$a_1' + e'$	Three Ni 4p	$a_2'' + e''$
Three Ni $3d_{x^2-y^2}$	$a_1' + e'$	Three Ni $3d_{yz}$	$a_2'' + e''$
Three Ni $4p_x$	$a_2' + e'$	Two Mo σ orbitals	$a_1' + a_2''$
Three Ni $3d_{xz}$	$a_2' + e'$	Four Mo $d\pi$ orbitals	$e' + e''$

to the geometry of the planar Re_3Cl_6 part of the $[Re_3Cl_{12}]^{3-}$ anion,[67] it is assumed initially that each nickel atom has two equivalent orbitals pointed in opposite directions perpendicular to the trinickel plane (which in the case of the $[Re_3Cl_{12}]^{3-}$ anion would point toward the two out-of-plane terminal chlorine atoms attached to each rhenium atom). Hence, each $M(CO)_5$ group can be considered to be bonded to a cyclopropenyl-like trinickel ring system which occupies one coordination site.[68] In order for the metal atom in each $M(CO)_5$ system to attain a closed-shell electronic configuration, the trinickel ring system can be considered as a two-electron donor with the electron pair formally donated from the trinickel ring to the $M(CO)_5$ group residing in the a_1 bonding combination formed by overlap of the octahedral-like σ orbital of the $M(CO)_5$ system with the a_1 symmetry combination of the three trinickel orbitals. Each $M(CO)_5$ fragment possesses two filled d_π metal orbitals of e representation which can interact with the corresponding two trinickel antibonding e orbital combinations; if these latter orbitals are presumed to be empty (which is later argued not to be the case), they provide a possible pathway for back-donation of charge from each $M(CO)_5$ fragment onto the $Ni_3(CO)_6$ part of the anion. However, the observed M–CO bond lengths strongly indicate that each of these filled e orbitals of the $M(CO)_5$ fragment is primarily utilized for back-bonding to the apical carbonyl ligand and to the appropriate trans pair of four equatorial carbonyl ligands. The Mo–CO(apical) distance of 1.903 (13) Å is 0.093 (19) Å shorter than the average Mo–CO(equatorial) distance of 1.996 Å; in the tungsten analog the corresponding difference in bond lengths is 0.053 (21) Å. This evidence that the filled e orbitals of each $M(CO)_5$ fragment are used primarily for carbonyl back-bonding rather than for any back-bonding to the trinickel system implies that each $M(CO)_5$ fragment is mainly linked to the three nickel atoms by only one delocalized electron-pair bond. It follows that each M–Ni bond distance should be considerably longer than a normal single-bond M–Ni distance. This expectation is in accord with the observed Mo–Ni and W–Ni distances, both of average value 3.10 Å, in that this distance is 0.3 Å longer than the calculated electron-pair Mo–Ni distance of 2.8 Å based on the sum of a mean Mo radius of 1.6 Å (obtained from half the Mo–Mo bond length of 3.22 Å in $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$[60] and 3.12 Å in $[PPN]_2[Mo_2(CO)_{10}]\cdot CH_2Cl_2$[51]) and a mean Ni radius of 1.2 Å (obtained from half the observed Ni–Ni distances of 2.39 Å in $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$,[69,70] 2.33 Å in $Ni_2(h^5\text{-}C_5H_5)_2$-

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(67) (a) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc., London*, 116 (1963); (b) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Amer. Chem. Soc.*, 85, 1349 (1963); *Inorg. Chem.*, **2**, 1166 (1963).

(68) A recent X-ray structural determination [D. L. Weaver and R. M. Tuggle, *J. Amer. Chem. Soc.*, **91**, 6506 (1969)] of $Ni[\pi\text{-}C_3(C_6H_5)_3]Cl(py)_2]\cdot py$ has shown that the triphenylcyclopropenyl ring can be considered to occupy one coordination site, the resulting four-coordinated geometry about the nickel atom in this complex being a distorted tetrahedron.

(69) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," Macmillan, New York, N. Y., 1961, p 640.

(70) V. A. Uchtman, Ph.D. Thesis, University of Wisconsin (Madison), 1968.

$(C_6H_5C_2C_6H_5)_2$,[71] 2.36 Å in $Ni_2(h^5\text{-}C_5H_5)_2(CO)_2$,[71] and 2.495 Å in $Ni_5(h^5\text{-}C_5H_5)_4S_4$[72]).

In order that the orbital types and transformational scheme involved in the trinickel interactions with the two $M(CO)_5$ fragments be analogous to those utilized in the $[Re_3Cl_{12}]^{3-}$ anion[63] and $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$,[64] local right-handed Cartesian coordinate systems can be chosen at each nickel atom, with the z axis directed to the center of the nickel triangle, the y axis perpendicular to the trinickel plane, and the x axis in this plane perpendicular to the y and z axes. A local right-handed coordinate system also is defined at each molybdenum atom, with the positive z axis directed toward the center of the nickel triangle and the x and y axes along the M–CO(equatorial) directions. For these particular choices of axes the resulting metal valence-orbital combinations for the M_2Ni_3 fragment of the $[M_2Ni_3(CO)_{16}]^{2-}$ anions are classified in Table V according to the irreducible representations of the D_{3h} point group. The nickel–carbonyl σ bonding of representations $2a_1' + a_2' + 3e'$ may be assumed as localized interactions which involve from overlap considerations primarily the valence 4s, $4p_x$, and $4p_z$ atomic orbitals of each nickel atom. For σ and π binding to the two molybdenum atoms of representations $a_1' + a_2'' + e' + e''$, it is apparent that for each nickel atom the $3d_{x^2-y^2}$ atomic orbital and either the $4p_y$ or $3d_{yz}$ atomic orbital (or a hybridized combination) possess the required symmetry (Table V) and directional properties for effective interaction. For the purpose of simplicity, it is arbitrarily assumed that this $3d_{yz}$–$4p_y$ pair does not hybridize and furthermore that only the $4p_y$ orbital is utilized along with the $3d_{x^2-y^2}$ orbital for bonding to the two molybdenum atoms. Although these assumptions cannot be correct in terms of a quantitative approach to the electronic structure, they have no effect on the results gleaned from this qualitative bonding description.

The equivalent orbital representation, which can be readily obtained by hybridization of the $4p_y$ and $3d_{x^2-y^2}$ atomic orbitals on each nickel atom, is initially assumed as an appropriate model to depict in a localized fashion the cyclopropenyl-like trinickel interaction with each $M(CO)_5$ fragment. Subsequently, it is shown that a more conceptually satisfying delocalized MO model which conforms to all of the experimental data is obtained when these orbitals are treated as separate basis functions. The remaining four 3d nickel atomic orbitals which are available for nickel–nickel interactions in the $Ni_3(CO)_6$ fragment are combined under D_{3h} symmetry to give *six* bonding symmetry orbitals (*viz.*, $d_{z^2}(a_1')$, $d_{xz}(e')$, $d_{yz}(a_2'')$, and $d_{xy}(e'')$) and *six* antibonding symmetry orbitals (*viz.*, $d_{xy}(a_1''^*)$, $d_{yz}(e''^*)$, $d_{xz}(a_2'^*)$, and $d_{z^2}(e'^*)$) relative to the isolated atomic orbitals of each nickel atom. After allowance for nickel–carbonyl σ bonding with the initially formulated premise that only four electrons are furnished to the pair of cyclopropenyl-like nickel orbitals for interaction with the corresponding orbitals of the two $M(CO)_5$ groups, there remain 22 electrons in the $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W) to be further considered for metal–metal interactions in the M_2Ni_3 cluster system. Although the degree of mixing which can occur among the trinickel metal symmetry orbitals belonging to the same irreducible representation is unknown such that in general the atomic orbital character of the energy levels cannot be specified, only the nature of the highest two energy levels (comprised of three antibonding orbitals) is of particular importance. These two energy levels for this triangular trinickel system would seem to be analogous, from orbital overlap considerations, to the corresponding levels for the triangular trimetal system in $Co_3(CO)_9X$ (X = S, Se)[66,73,74] of C_{3v} geometry and in $Ni_3(h^5\text{-}C_5H_5)_3S_2$[65] and $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$[69,70] of D_{3h} geometry. The highest two energy levels for these latter three molecules were experimentally established from a combination of single-crystal esr and X-ray diffraction studies [65,66,70,73,74] as primarily the in-plane antibonding σ^* metal–metal orbitals which in MO language for D_{3h} symmetry essentially comprise the in-plane nondegenerate $d_{xz}(a_2'^*)$ and doubly degenerate $d_{z^2}(e'^*)$ orbitals. The addition of 18 of the 22 available electrons to the *other 9* orbitals results in *6* electrons occupying the three corresponding lowest energy in-plane *bonding* $d_{z^2}(a_1')$ and $d_{xz}(e')$ nickel symmetry orbitals. The other 12 of 18 electrons fill both the bonding and antibonding levels $d_{yz}(a_2'')d_{xy}(e'')^4d_{xy}(a_1''^*)^2d_{yz}(e''^*)^4$ which consequently are reasonably presumed to cancel one another's bonding. Hence, the *occupation* of the in-plane *bonding* $d_{z^2}(a_1')$ and $d_{xz}(e')$ orbitals with *six* electrons together with the corresponding in-plane *antibonding* $d_{xz}(a_2'^*)$ and $d_{z^2}(e'^*)$ combinations being *empty* is mathematically equivalent[75] under the perfect-pairing approximation in a valence-bond formalism to the formation of localized electron-pair Ni–Ni bonds.

It is found that the placement of the remaining *four* electrons in the out-of-plane M–Ni orbitals rather than in the antibonding in-plane $d_{xz}(a_2'^*)$ and $d_{z^2}(e'^*)$ nickel orbital combinations conforms to the experimental bond lengths of the M_2Ni_3 cluster system (including the observed deformation from a D_{3h} to a C_{3v} geometry) as well as to the observed diamagnetic character of the $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W).

On the basis of the determined energy ordering in $Co_3(CO)_9X$ (X = S, Se),[66,74] $Ni_3(h^5\text{-}C_5H_5)_3S_2$,[65] and $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$,[66,70] the assignment of the four extra electrons to the in-plane antibonding σ^* trinickel orbitals of the planar $Ni_3(CO)_6$ system would result in the energy order $d_{xz}(a_2'^*)^2d_{z^2}(e'^*)^2$; this electronic configuration containing two unpaired electrons is incompatible with the diamagnetic behavior of the anions (unless there is sufficient breakdown of the degenerate $d_{z^2}(e'^*)^2$ orbitals due to the actual symmetry of the entire anion to give spin pairing). A much more convincing rationalization against the allocation of the four remaining electrons to the three antibonding in-

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(71) O. S. Mills and B. W. Shaw, *J. Organometal. Chem.*, 11, 595 (1968).

(72) H. Vahrenkamp and L. F. Dahl, *Angew. Chem., Int. Ed. Engl.*, 8, 144 (1969).

(73) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 6, 1229 (1967); D. L. Stevenson, C. H. Wei, and L. F. Dahl, submitted for publication.

(74) C. E. Strouse and L. F. Dahl, submitted for publication.

(75) Hybrid combinations of the d_{z^2} and d_{xz} atomic orbitals on each nickel atom produce two equivalent nickel orbitals which can form localized electron-pair Ni–Ni σ bonds by overlap with the corresponding identical hybrid orbitals on the two other nickel atoms. The six electrons are added to the three bonding combinations of the three localized pairs of interacting equivalent orbitals to produce the three electron-pair Ni–Ni bonds.

plane $d_{xz}(a_2'^*)$ and $d_{z^2}(e'^*)$ symmetry orbitals of the $Ni_3(CO)_6$ system emerges from the fact that the resulting *net* stabilization of the trinickel system by direct Ni–Ni interactions would be due to only *two* bonding electrons (*i.e.*, six bonding minus four antibonding), which would lead in valence-bond terminology to a Ni–Ni bond order of *less* than one. Yet the observed Ni–Ni distances of average value 2.34 Å in both the $[Mo_2Ni_3(CO)_{16}]^{2-}$ and $[W_2Ni_3(CO)_{16}]^{2-}$ anions are in the expected single-bond range rather than corresponding to the much longer metal–metal bond lengths found in the triangular metal complexes $Co_3(CO)_9S$ (2.637 (7) Å),[73] $Ni_3(h^5\text{-}C_5H_5)_3S_2$ (2.801 (5) Å),[65] and $Co_3(h^5\text{-}C_5H_5)_3S_2$ (2.687 (7) Å),[76] all of which contain excess electrons in these antibonding in-plane σ^* trimetal orbitals.

The only alternative allotment of the four electrons is to the out-of-plane doubly degenerate cyclopropenyl-like antibonding trinickel orbitals. In order to demonstrate the occurrence of a diamagnetic ground state for such an electronic assignment, it is necessary to utilize the *separated* $3d_{x^2-y^2}$ and $4p_y$ trinickel symmetry orbitals rather than hybridized equivalent orbitals of these basis functions for interaction with the two octahedral-like σ-orbital combinations of the two molybdenum atoms. A qualitative energy correlation diagram of this Ni–M bonding interaction is given in Figure 6 for both the idealized D_{3h} geometry and observed distorted C_{3v} geometry of the M_2Ni_3 cluster system. Under D_{3h} symmetry four of the eight available electrons (*viz.*, comprised of the above-mentioned four extra electrons plus four electrons from the two electron pairs formally donated in the equivalent orbital representation from the trinickel ring to the two $M(CO)_5$ fragments) expectedly fill the $1a_1'$ and $1a_2''$ M–Ni bonding levels corresponding in the equivalent orbital picture to the two delocalized electron-pair a_1 M–Ni bonds; the other four electrons then fully occupy the e′ level which under D_{3h} symmetry has no $4p_y$ orbital character.[77] The deformation of the M_2Ni_3 fragment from D_{3h} to C_{3v} symmetry may be attributed to an elongation of the M–Ni bonds by 0.10 Å on one side of the trinickel plane relative to the M–Ni bonds on the other side due to electron–electron repulsions with the filled d_π orbitals on the two molybdenum atoms. A greater stabilization in the $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W) apparently is achieved by the preferential accumulation of charge density on the particular side of the trinickel plane containing the longer M–Ni bond lengths rather than equivalent electron-density distribution on both sides under a D_{3h} geometry. This asymmetry of charge in the M_2Ni_3 cluster permits under a C_{3v} geometry the mixing of $4p_y$ nickel orbital character with the $d_{x^2-y^2}$ nickel orbitals, thereby causing an energetic stabilization of the four electrons in the resulting degenerate e orbitals. It is noteworthy that this filled orbital is *antibonding* with respect to mixing with the filled d_π $M(CO)_5$ orbitals of e representation unless back-bonding into the π^* carbonyl orbitals of the two $M(CO)_5$ groups sufficiently depletes the electron density localized in the d_π orbitals of the M atoms that a net bonding charge transfer occurs from the central e orbitals of the $Ni_3(CO)_6$ fragment to the d_π $M(CO)_5$ orbitals. This bonding description presumes that the least stable electrons are antibonding with respect to the M–Ni interactions, and hence if any electrons can be moved from the anion by oxidation, the molecular parameters of the oxidized species should show a decrease in the M–Ni distances corresponding to greater M–Ni bonding character.

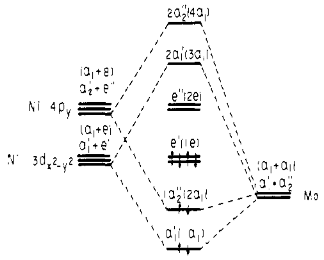

Figure 6. Qualitative energy correlation diagram showing interactions of the two Mo σ-orbital combinations with the appropriate trinickel symmetry orbital combinations. Irreducible representations are given without parentheses for an idealized D_{3h}-$\bar{6}2m$ geometry and with parentheses for the observed C_{3v}-$3m$ geometry of the M_2Ni_3 cluster system of the $[M_2Ni_3(CO)_{16}]^{-2}$ anions (M = Cr, Mo, W). Placement of eight available electrons leads to a diamagnetic ground state. Under C_{3v} symmetry the $3d_{x^2-y^2}$ and $4p_y$ trinickel symmetry orbital combinations belonging to the same irreducible presentation can mix, thereby energetically stabilizing the M_2Ni_3 part of the anions.

The application of this MO model shows that these anions are typical of metal carbonyl cluster systems in containing electrons in antibonding as well as bonding metal symmetry orbitals. The overall stability of this metal carbonyl cluster system no doubt is largely due to the use of the empty π^* carbonyl orbitals to delocalize electronic charge from the metal symmetry orbitals, particularly from the higher energy antibonding ones which are nearer in energy to the empty carbonyl π^* orbital combinations.

Discussion of the Reactions and Stereochemical Implications. The determined structure of the $[M_2Ni_3(CO)_{16}]^{2-}$ anions (M = Cr, Mo, W) with its long Ni–M bond lengths indicative that the two $M(CO)_5^-$ groups are weakly linked to the central neutral $Ni_3(CO)_6$ fragment provides a rational basis for the observed chemical degradation of $[PPN]_2[W_2Ni_3(CO)_{16}]$ to give either the $[W_2(CO)_{10}]^{2-}$ anion and/or the $[W(CO)_5Cl]^-$ anion. It is noteworthy that in none of these reactions has any trace of a nickel carbonyl derivative ever been observed. Furthermore, attempts to prepare analogous $[M_2Ni_3(CO)_{16}]^n$ cluster systems by such reactions as those between $Ni(CO)_4$ and either $[WMn(CO)_{10}]^-$ or $Mn_2(CO)_{10}$ in refluxing THF (over a 1-2-hr period) have not as yet been successful.

If one assumes in the observed chemical reactions that dissociation of the $[W_2Ni_3(CO)_{16}]^{2-}$ anion occurs to give two radical $W(CO)_5^-$ anions and a neutral $Ni_3(CO)_6$ species, then the former paramagnetic anion can either dimerize or abstract a chlorine atom from a chlorinated solvent (*e.g.*, methylene chloride) or $HgCl_2$ to give the $[W(CO)_5Cl]^-$ anion. Although the planar D_{3h} $Ni_3(CO)_6$-type structure is as yet unknown for any complexes of nickel, this particular kind of neutral trinuclear metal cluster system was first isolated and

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(76) P. D. Frisch and L. F. Dahl, to be published.

(77) The trinickel orbitals contributing to the filled $1a_1'$ and $1a_2''$ M–Ni bonding orbitals are also bonding with respect to the trinickel system, while the filled e′ M–Ni orbitals are antibonding with respect to the trinickel system.

characterized by Booth, Chatt, and Chini[78] and later ascertained from an X-ray study[79] for a metal phosphine carbonyl complex of the congener platinum, *viz.*, $Pt_3\{P(C_6H_5)_2(CH_2C_6H_5)\}_3(CO)_3$; in this complex as in the hypothetical electronically equivalent neutral $Ni_3(CO)_6$ species, each metal atom has only a 16-electron count (*i.e.*, 2 electrons less than the required number for a closed-shell electronic configuration). The fact that other platinum phosphine cluster systems such as $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$[80] and $Pt_3\{P(C_6H_5)_3\}_4(CO)_3$[81] have also been shown from X-ray studies to contain analogous planar five-coordinated platinum atoms (*i.e.*, linked with one terminal ligand, two bridging carbonyl groups, and two other platinum atoms), whereas no corresponding complexes containing five-coordinated nickel atoms are known, is completely consistent with the expected large instability (and nonisolation to date) of the $Ni_3(CO)_6$ fragment or any other trinickel analog.

Further work is in progress on the derivative chemistry of these new cluster systems.

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(78) G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965); J. Chatt and P. Chini, *J. Chem. Soc. A*, 1538 (1970).

(79) P. M. Cook, L. F. Dahl, P. Chini, and J. Chatt, to be submitted for publication.

(80) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, 91, 1574 (1969).

(81) C. E. Strouse, R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, to be submitted for publication.

Pulse Radiolysis of Aqueous Solutions of Pentacyanocobaltate(II). The Detection and Characterization of Pentacyanocobaltate(I)

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Abstract: Hydrated electrons, generated by pulse radiolysis of aqueous solutions of pentacyanocobaltate(II), react with the latter to form a transient species identified as pentacyanocobaltate(I), *i.e.*, $Co(CN)_5{}^{3-} + e^-{}_{aq} \rightarrow Co(CN)_5{}^{4-}$. The further reaction of pentacyanocobaltate(I) with water yields hydridopentacyanocobaltate(III), according to $Co(CN)_5{}^{4-} + H_2O \rightarrow Co(CN)_5H^{3-} + OH^-$. Kinetic measurements on the two successive reactions yielded the rate constants $1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$ and $1.1 \times 10^5\ sec^{-1}$, respectively. The spectrum of $Co(CN)_5{}^{4-}$ is described and some aspects of its chemistry are discussed.

This paper describes pulse radiolysis studies on aqueous solutions of $Co(CN)_5{}^{3-}$, including kinetic measurements on the formation of $Co(CN)_5{}^{4-}$ according to eq 1 and on the further reaction of $Co(CN)_5{}^{4-}$

$$Co(CN)_5{}^{3-} + e^-{}_{aq} \xrightarrow{k_1} Co(CN)_5{}^{4-} \qquad (1)$$

with water to form $Co(CN)_5H^{3-}$ according to eq 2.[1]

$$Co(CN)_5{}^{4-} + H_2O \xrightarrow{k_2} Co(CN)_5H^{3-} + OH^- \qquad (2)$$

$Co(CN)_5{}^{4-}$ has previously been postulated as an intermediate in the chemical[2–4] and electrochemical[5] oxidations of $Co(CN)_5H^{3-}$, as well as in the electrochemical reduction of $Co(CN)_5{}^{3-}$.[6] However, this appears to be the first time that this species has been directly observed and spectrally characterized.

Experimental Section

Hydrated electrons ($e^-{}_{aq}$) were generated in the aqueous solutions by pulsed electron irradiation with the Argonne National Laboratory's ARCO linear accelerator (linac), in accord with the general procedures described elsewhere.[7,8] The electron pulses, of approximately 15-MeV energy and of 0.4-μsec duration, were attenuated by passing through quartz diffusors to vary the beam intensity and to achieve more uniform solution irradiation. The dose per pulse (determined by measuring the charge collected on a Faraday cup placed in front of the cell) was typically of the order of 1 krad, resulting in $e^-{}_{aq}$ concentrations in the micromolar range. The irradiations were performed in a 5-cm cylindrical cell with Suprasil

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(1) A preliminary account of this and related work has previously appeared: G. D. Venerable II, E. J. Hart, and J. Halpern, *J. Amer. Chem. Soc.*, 91, 7538 (1969).

(2) A. A. Vlček and J. Hanzlik, *Inorg. Chem.*, 6, 2053 (1967).

(3) H. S. Lim and F. C. Anson, *ibid.*, 10, 103 (1971).

(4) J. Halpern and M. Pribanić, to be published.

(5) J. Hanzlik and A. A. Vlček, *Chem. Commun.*, 47 (1969).

(6) A. A. Vlček, *Pure Appl. Chem.*, 10, 61 (1961).

(7) A. S. Ghosh-Mazumdar and E. J. Hart, *Advan. Chem. Ser.*, No. 81, 193 (1968), and references therein.

(8) B. D. Michael and E. J. Hart, *J. Phys. Chem.*, 74, 2878 (1970).