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Received December 12, 1973

Synthesis and Structure of a Hexanuclear Nickel Carbonyl Dianion, [Ni₃(CO)₃(μ₂-CO)₃]₂²⁻, and Comparison with the [Pt₃(CO)₃(μ₂-CO)₃]₂²⁻ Dianion. An Unprecedented Case of a Metal Cluster System Possessing Different Metal Architectures for Congener Transition Metals[1]

Sir:

We wish to report the isolation and structural characterization of the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion which represents the first unambiguous example of a hexanuclear metal carbonyl cluster system with 12 ligands. Of prime importance to the field of metal carbonyl chemistry is that this research combined with the subsequent preparation and structural analysis[2] of the hexaplatinum carbonyl analog, $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$, has established for the first time that direct metal–metal interactions involving a first-row transition metal can be sufficiently different from those involving a congener third-row transition metal such as to give rise to two different metal frameworks which are conformers of each other.[3,4]

Prior to this work, the syntheses of various nickel carbonyl anions formulated as $[Ni_2(CO)_6]^{2-}$, $[Ni_3(CO)_8]^{2-}$, $[Ni_4(CO)_9]^{2-}$, and $[Ni_5(CO)_9]^{2-}$ have been reported[5] in the literature. Since the stoichiometries of these unusual polymeric species cannot be unequivocally characterized by the usual chemical and physical methods, a reinvestigation of the nickel carbonyl anions has been initiated involving X-ray diffraction studies to ascertain their formulas as well as to obtain definitive

information concerning the structural interrelationships and bonding of the complexes.

The $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion was prepared by reduction of nickel tetracarbonyl. The reduction reaction is extremely dependent on the reducing agent used and upon the experimental conditions with infrared solution spectra providing evidence for at least six different anionic species, of which one of intense red color predominates on account of its relative ease of formation and stability to hydrolysis. For example, this anion can be prepared through the reduction of $Ni(CO)_4$ either with sodium metal in THF (60°, 20 hr) or with potassium hydroxide in methanol (55°, 5 hr). Evaporation of solvent followed by redissolution in water and saturation with solid potassium bromide yields the potassium salt in a crystalline dark red form (*ca.* 25–60% yield). The corresponding tetramethylammonium salt, obtained from metathesis of the potassium salt in water and recrystallized from acetone-isopropyl alcohol, is diamagnetic[6] and moderately stable in air. An infrared spectrum of the sodium salt in THF solution reveals carbonyl absorption bands at 1975 (s), 1810 (m), 1790 (m), and 1743 (w) cm⁻¹; the reasonable agreement of these values with those previously reported[7] for the sodium salt of the presumed $[Ni_4(CO)_9]^{2-}$ anion (*viz.*, 1985 (s), 1818 (ms), and 1799 (ms) cm⁻¹ in THF solution) offers convincing evidence that the two anions may in fact be identical. Since our elemental analyses instead suggested an empirical formula of $[Ni_3(CO)_6]_n{}^{n-}$, its actual composition as a $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion was ascertained from an X-ray diffraction analysis of the tetramethylammonium salt.[8,9]

This dianion of crystallographic $C_{3i}\text{-}\bar{3}$ site symmetry has an idealized $D_{3d}\text{-}32/m$ geometry (Figure 1) which may be envisioned as a trigonal-antiprismatic array of metal atoms formed from the dimerization of two planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties through direct Ni–Ni interactions involving the two additional anionic electrons.

The symmetry-related Ni–Ni bonds within both Ni₃-(CO)₆ triangles are 2.38 Å in length, while the other six equivalent Ni–Ni bonds between them are 2.77 Å. This elongated distortion of the octahedron of nickel atoms along the crystallographic threefold axis thereby results in two smaller transoid, equilateral triangular metal faces, whose edges are symmetrically bridged by carbonyls, and six isosceles triangular faces with two longer edges. The two independent Ni–CO(bridging) bond lengths are both 1.90 Å which is 0.25 Å longer than the one independent Ni–CO(terminal) bond length of 1.75 Å; the bridging and terminal C–O distances are 1.17 and 1.13 Å, respectively.

The transformation from a trigonal-antiprismatic (or octahedral-like) metal arrangement in $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion to a trigonal-prismatic one in the cor-

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

(2) J. C. Calabrese, P. Chini, L. F. Dahl, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, 96, 2614 (1974).

(3) Previously determined structural dissimilarities between polynuclear metal carbonyl complexes (of the same general formula) for first-row transition metals compared to those for third-row transition metals have involved different arrangements of carbonyl ligands, *e.g.*, Fe₃(CO)₁₀(μ₂-CO)₂ *vs.* Os₃(CO)₁₂ and Co₄(CO)₉(μ₂-CO)₃ *vs.* Ir₄(CO)₁₂.

(4) P. Chini, *Inorg. Chim. Acta Rev.*, 2, 31 (1968).

(5) *Cf.* F. Calderazzo, R. Ercoli, and G. Natta in "Organic Synthesis Via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 68–70, and references cited therein.

(6) We are indebted to Mr. James Kleppinger at the University of Wisconsin (Madison) for making the magnetic susceptibility measurements *via* the Faraday method.

(7) W. Hieber and J. Ellermann, *Z. Naturforsch. B*, 18, 595 (1963).

(8) [N(CH₃)₄]₂[Ni₃(CO)₃(μ₂-CO)₃]₂: trigonal, $P\bar{3}$; $a = b = 11.003$ (1), $c = 7.045$ (1) Å; $V = 738.7$ Å³; $\rho_{calcd} = 1.88$ g cm⁻³ for $Z = 1$. Anisotropic least-squares refinement gave $R_1(F) = 3.9\%$ and $R_2(F) = 4.0\%$ for 614 independent diffractometer data ($I > 2\sigma(I)$).

(9) For computation of distances and bond angles, see paragraph at end of paper regarding supplementary material.

responding platinum analog, $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$, represents the first known instance that metal–metal interactions involving first-row transition metals can be sufficiently different from those involving third-row transition metals such as to produce two different metal architectures which are conformers of each other. This conformational change, by which in the *trigonal prismatic* cluster system each metal atom in one planar $M_3(CO)_3(\mu_2\text{-}CO)_3$ fragment is only bonded to *one* corresponding metal atom in the other identical fragment in contradistinction to each metal atom in the *trigonal-antiprismatic* cluster system being coordinated to *two* metal atoms in the opposite fragment, presumably reflects from a viewpoint of total energy minimization the inherently greater strength of a given kind of Pt–Pt bond *vs.* a corresponding Ni–Ni bond such that a trigonal prismatic conformation (with only three *inter*triangular Pt–Pt bonds of a given type) is stabilized in the solid state for the $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion.[10] The marked difference between the much longer *inter*triangular Pt–Pt distances of 3.04 Å in the prismatic platinum cluster *vs.* the corresponding Ni–Ni distances of 2.77 Å in the antiprismatic nickel cluster is in accord with the premise that repulsive forces between the two halves of the dianion sufficiently increase at the smaller Ni–Ni distance to give the staggered conformation.

Since the metal–metal interactions within each $M_3(CO)_3(\mu_2\text{-}CO)_3$ fragment in both the nickel and platinum clusters are presumed to correspond to normal electron-pair bonds,[11,12] the similarity of the ratio for these (Ni–Ni) to (Pt–Pt) bond lengths within the $M_3(CO)_6$ triangles of $2.38\text{Å}/2.66\text{Å} = 0.89$ to the corresponding ratio of $2.77\text{ Å}/3.04\text{ Å} = 0.91$ for the metal–metal distances between the two $M_3(CO)_6$ triangles suggests that the conformational change from an antiprismatic metal array to a prismatic one has no appreciable effect on the *inter*triangular metal–metal distances.

As an initiate to the homologous series of hexanuclear metal carbonyl complexes which possess an *octahedral* (or *trigonal-antiprismatic*) metal arrangement and an electronically equivalent configuration of 86 valence electrons available for metal–metal and metal–ligand bonding, the $[Ni_6(CO)_{12}]^{2-}$ dianion represents the first such member with only 12 ligands.[13,14] Previous struc-

$[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$

Figure 1. Architecture of the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion which possesses crystallographic site symmetry $C_{3i}\text{-}\bar{3}$; its geometry experimentally conforms to $D_{3d}\text{-}\bar{3}2/m$ symmetry with the six nickel atoms at the vertices of a trigonal antiprism.

turally ordained members include $Ru_6(CO)_{18}H_2$,[15a] $M_6(CO)_{16}$ (M = Co,[15b] Rh,[15c] Ir[15d]), $[M_6(CO)_{15}]^{2-}$ dianions (M = Co,[15e] Rh,[15d,f] Ir[15d]), $[M_6(CO)_{14}]^{4-}$ tetraanions (M = Co,[15g] Rh[15h]), and the $[Ni_2Co_4\text{-}(CO)_{14}]^{2-}$ dianion[15i] as well as the carbidocarbonyl $[Fe_6(CO)_{16}C]^{2-}$ dianion,[15j] $Ru_6(CO)_{17}C$,[15k] and $Ru_6(CO)_{14}(arene)C$.[15l] The corresponding isoelectronic $[Pt_6(CO)_{12}]^{2-}$ dianion is the second member of the hexanuclear metal carbonyl complexes possessing a trigonal-prismatic metal arrangement, the other member being the carbidocarbonyl hexarhodate dianion,[16] $[Rh_6(CO)_6(\mu_2\text{-}CO)_9C]^{2-}$, which, with the carbide atom at the center of the prism and symmetrically bridging carbonyl groups spanning the polyhedral metal edges, further differs from the $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion in that its electronic configuration involving metal–metal interactions conforms to a so-called electron-precise metal polyhedron. An outline of a qualitative molecular orbital representation utilized for an octahedral-like metal carbonyl cluster system with 86 valence electrons has been given elsewhere.[15e]

The above work suggests that some of the other non-characterized nickel carbonyl anions may likewise contain $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragments. As an operational test of this hypothesis, crystalline salts of other nickel

(10) *Cf.* F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969). An illustration of the much more robust character of Pt–Pt bonding in coordination compounds is given by platinum bis(ethylene-1,2-dithiolene) being a (metal–metal)-bonded dimer with a short Pt–Pt distance of 2.77 Å in contrast to the corresponding planar $Ni(S_2C_2H_2)_2$ molecule being monomeric with no exceptionally close intermolecular contacts: K. W. Browall, L. V. Interrante, and J. S. Kasper, *J. Amer. Chem. Soc.*, **93**, 6289 (1971). An intriguing problem, which may be resolved from temperature-dependent nmr measurements, is whether the $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion is a stereochemically nonrigid species which can undergo interconversion in solution from a trigonal prismatic to a trigonal antiprismatic conformation by internal rotation about the principal threefold axis.

(11) Although a planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ type component is not known *per se*, such a fragment is contained in the recently synthesized $[M_2Ni_3(CO)_{14}(\mu_2\text{-}CO)_3]^{2-}$ dianions (M = Cr, Mo, W)[12] in which it is symmetrically capped on both sides by two apical $M(CO)_5$ groups to give a trigonal bipyramidal metal framework. Despite a crystal disorder which results in relatively large uncertainties in the positional parameters of the $Ni_3(CO)_6$ fragment, the observed Ni–Ni distances of 2.34 Å (av) in both the dimolybdenum–trinickel and ditungsten–trinickel dianions are comparable to that found in the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion. A proposed qualitative MO description[12] of the bonding corresponds to normal electron-pair metal–metal interactions within the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment and delocalized, multicentered metal–metal interactions involving this trimetal fragment and the two $M(CO)_5$ groups.

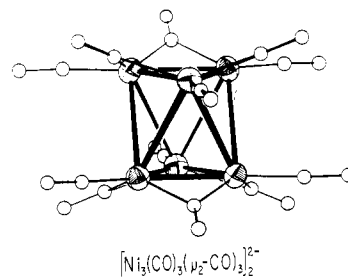(12) J. K. Ruff, R. P. White, Jr., and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 2159 (1971).

(13) This stereochemistry offers additional support for the proposed arrangement of hydrogen atoms (which were not located from the X-ray diffraction study) in the $Cu_6(P(C_6H_5)_3)_6H_6$ molecule.[14] The six copper atoms, to each of which is bonded a terminal triphenylphosphine ligand, are arranged at the vertices of an octahedron which is moderately distorted such that two mutually trans octahedral faces are enlarged with Cu–Cu edges of 2.66 Å relative to the other six Cu–Cu edges of 2.54 Å. The postulated molecular configuration[14] of this hexanuclear copper hydride cluster with the six hydrogen atoms symmetrically bridging the six long Cu–Cu edges is structurally analogous with that of the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion. These stereochemistries are in complete harmony with the well-documented observations that bridging carbonyls give rise to shorter metal–metal bond lengths whereas bridging hydride ligands produce longer metal–metal bond lengths.

(14) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972).

(15) (a) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970); M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 5670 (1971); (b) V. Albano, P. Chini, and V. Scatturin, *Chem. Commun.*, 163 (1968); (c) E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, **85**, 1202 (1963); (d) L. Malatesta, G. Caglio, and M. Angoletta, *Chem. Commun.*, 532 (1970); (e) V. Albano, P. Chini, and V. Scatturin, *J. Organometal. Chem.*, **15**, 423 (1968); (f) S. Martinengo and P. Chini, unpublished results; (g) V. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organometal. Chem.*, **16**, 461 (1969); (h) P. Chini and S. Martinengo, *Chem. Commun.*, 1092 (1969); (i) P. Chini, A. Cavalieri, and S. Martinengo, *Coord. Chem. Rev.*, **8**, 3 (1972); (j) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, **93**, 3073 (1971); (k) A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Commun.*, 596 (1969); (l) R. Mason and W. R. Robinson, *ibid.*, 468 (1968).

(16) V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 651 (1973).

carbonyl anions have been isolated and structural studies are in progress.

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Kinetics and Mechanism of the Reaction between Chromium(II) and Pentaaquo(diiodomethyl)chromium(III) Ion (Cr(OH₂)₅CHI₂²⁺). Evidence for a Carbon-Bridged Dinuclear Chromium Intermediate

Sir:

Pentaaquo(diiodomethyl)chromium(III) ion, abbreviated $CrCHI_2^{2+}$, can be prepared by the reaction between excess iodoform and chromium(II); however, when excess chromium(II) is used, pentaaquo(iodomethyl)chromium(III) ion, abbreviated $CrCH_2I^{2+}$, is identified as a major product.[1] We wish to report results of our study of the reaction between $CrCHI_2^{2+}$ and Cr^{2+}, which provides evidence for a carbon-bridged dinuclear chromium intermediate.

The reduction of $CrCHI_2^{2+}$ by Cr^{2+} produces $CrCH_2I^{2+}$ quantitatively according to the equation

$$2Cr^{2+} + CrCHI_2^{2+} + H^+ = CrI^{2+} + Cr^{+3} + CrCH_2I^{2+} \quad (1)$$
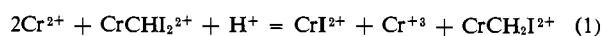
If excess Cr^{2+} is used, the $CrCH_2I^{2+}$ will be further reduced to Cr^{3+} and CH_4, although at a much slower rate than (1).[2]

The kinetics of eq 1 were followed by a titrimetric analysis of unreacted chromium(II).[3] Measured aliquots of the reaction mixture were injected into deoxygenated solutions of acidic Cr(VI); the resultant solution was then passed through a short column of cation-exchange resin. The negative Cr(VI) species were not retained in the resin and the decrease in absorbance

could then be determined without interfering absorbance by positive chromium complexes.

The disappearance of Cr^{2+} showed first-order dependence on $CrCHI_2^{2+}$ and Cr^{2+} and was independent of H^+. The rate constants were determined by a computer analysis based on the integrated rate law

$$\frac{1}{2A - B} \ln \frac{B(A - X)}{A(B - 2x)} = kt \quad (2)$$

where A = initial $[CrCHI_2^{2+}]$, B = initial $[Cr^{2+}]$, and $2x$ = $[Cr^{2+}]$ which has reacted. Plots of (2) were linear over 95% of the reaction and the rate constants are reported in Table I. The value of $\Delta H^{\neq}$ was cal-

Table I. Second-Order Rate Constants for the Reduction of $CrCHI_2^{2+}$ by Cr^{2+} ($-d[Cr^{2+}]/dt = k_1[CrCHI_2^{2+}][Cr^{2+}]$)

T, °C[a]	$[H^+]$, M[b]	k_1, M^{-1} sec^{-1} [c]
0	0.1	2.66 ± 0.13
0	0.5	2.77 ± 0.16
0	1.0	2.72 ± 0.14
5	0.1	3.29 ± 0.18
5	0.5	3.31 ± 0.17
5	1.0	3.38 ± 0.18
10	0.1	4.15 ± 0.23
10	0.5	4.09 ± 0.17
10	1.0	4.11 ± 0.19
15	1.0	5.08 ± 0.22

[a] Temperature error of ±0.05°. [b] Ionic strength maintained at 1.0 M by NaClO₄. [c] Determined by a linear least-squares computer analysis based on integrated second-order rate law.

culated to be 6.5 ± 0.5 kcal/mol and $\Delta S^{\neq}$ to be $-32 ±$ 1 eu. The calculated value of k at 25° is 11.2 M^{-1} sec^{-1}.

The appearance of CrI^{2+} as a product and the first-order dependence on Cr^{2+} and $CrCHI_2^{2+}$ is evidence that the rate-determining step of the reaction involves the abstraction of an iodine atom by Cr^{2+} by means of a bridged transition state $[Cr-CHI-I-Cr]^{4+}$. This reaction would produce $CrCHI \cdot ^{2+}$ which could rapidly react with Cr^{2+} to form the final products. The low $\Delta H^{\neq}$ is consistent with breaking a relatively weak C–I bond, and the negative $\Delta S^{\neq}$ is consistent with the formation of a highly charged transition state involving the aggregation of two ions.[4]

Isotopic labeling experiments on (1) were also carried out. In one series, labeled Cr^{2+} (^{51}Cr) was added to unlabeled $CrCHI_2^{2+}$. The label appeared in all the products.

$$2*Cr^{2+} + CrCHI_2^{2+} + H^+ = *CrI^{2+} + *Cr^{+3} + *CrCH_2I^{2+}$$
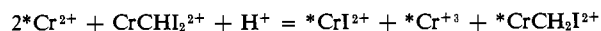
Similar results are obtained with labeling experiments involving $CrCHCl_2^{2+}$ and Cr^{2+}.[5] The label in the organochromium product can be readily explained by postulating a carbon-bridged dinuclear chromium intermediate $*[CrCHICr]^{4+}$ which can break either Cr–C bond to form the final products.[6]

In another series of experiments in which labeled $CrCHI_2^{2+}$ was added to unlabeled Cr^{2+}, a small amount

(1) D. Dodd and M. D. Johnson, *J. Chem. Soc. A*, 34 (1968).
(2) R. S. Nohr and L. O. Spreer, *Inorg. Chem.*, in press.
(3) R. V. James, Ph.D. Thesis, University of Colorado, 1969.

(4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 129.
(5) J. H. Espenson, private communication.
(6) When labeled Cr^{2+} is added to unlabeled $CrCHI_2^{2+}$ and the reaction is quenched before completion, no label appears in unreacted $CrCHI_2^{2+}$. Therefore the exchange $CrCH_2I^{2+} + *Cr^{2+} = *CrCH_2I^{2+} + Cr^{2+}$ must be dismissed as an explanation for the labeling experiments with $CrCHI_2^{2+}$ and Cr^{2+}.