hydroxy case this is presumably due to the same strong, dominating intraligand hydrogen-bond network in both isomers, which also keeps the adjacent OH^- ligands farther from each other.

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Registry No. IIa, 15663-27-1; IIb, 14913-33-8; IIIa, 20115-64-4; IIIb, 20115-65-5; IVb, 63700-88-9; IVc, 97805-43-1; Va, 54933-51-6; Vc, 54906-64-8; VI, 97732-33-7; VII, 17524-19-5.

Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

EPR Spectra and Structures of Three Binuclear Nickel Carbonyls Trapped in a Krypton Matrix: $Ni_2(CO)_8^+$, $Ni_2(CO)_7^-$, and $Ni_2(CO)_6^+$ [†]

J. R. MORTON* and K. F. PRESTON

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Three binuclear nickel carbonyl free radicals have been detected by EPR spectroscopy in a Kr matrix at 77 K. The observed spectra are tentatively assigned to the species $Ni_2(CO)_8^+$, $Ni_2(CO)_7^-$, and $Ni_2(CO)_6^+$, which have two, one, and two bridging carbonyls, respectively.

Introduction

In our studies of paramagnetic metal carbonyls, we recently turned our attention to the EPR spectra of cluster species. This topic was initiated with our investigation[1] of the binuclear manganese carbonyl $Mn_2(CO)_9^-$ in a single crystal of $Mn_2(CO)_{10}$. With the discovery[2] of $HCo_2(CO)_8$ and $Co_2(CO)_8^-$ as products of the γ irradiation of $HCo(CO)_4$ in Kr, it became apparent that clustering of metal carbonyls occurred in a krypton matrix at 77 K. The γ irradiation of metal carbonyls in Kr thus offered a potentially fruitful source of polynuclear carbonyl radicals for spectroscopic studies.

In the present article we discuss the structures of three binuclear nickel carbonyl radicals derived from $Ni(CO)_4$.

Experimental Section

Nickel tetracarbonyl was obtained from Alfa Inorganics; nickel metal enriched to 86% in the isotope ^{61}Ni was obtained from Oak Ridge National Laboratory and carbon monoxide enriched to 99% in ^{13}C from Merck Sharp and Dohme Ltd., Montreal, Canada.

$Ni(CO)_4$ enriched in ^{13}C was prepared by thermal decomposition of ordinary $Ni(CO)_4$ in a thick-walled glass tube. After the CO formed was removed, a small quantity of mercury was introduced, followed by excess ^{13}CO. When the tube was heated to 80 °C, at which temperature the pressure was approximately 1 MPa, $Ni(CO)_4$ enriched in ^{13}C was obtained. Enrichment with ^{61}Ni was carried out by reacting enriched metal with CO at 300 °C and 30 MPa with use of a droplet of mercury as a catalyst.

Two micromoles of $Ni(CO)_4$ and 2500 μmol of krypton (Matheson) were placed in a 4 mm o.d. Suprasil tube, which was sealed off under vacuum. The samples were annealed at −130 °C and then irradiated at 77 K in a 700-TBq ^{60}Co γ source.

EPR spectra were obtained at 77 K with a Varian E12 spectrometer equipped with accessories to measure the microwave frequency and the magnetic field. Spectral simulations were carried out with the aid of the Lefebvre–Maruani[5] or Belford[6] programs.

Results

Freshly irradiated samples of $Ni(CO)_4$ in krypton showed, at 77 K, spectra attributable to three species. A very strong signal at $g = 2.1425$ was labeled A but unfortunately could not be positively associated with any other features in the spectrum. Two weaker features at 1.9781 and 2.0000 were associated with species B, and a third species (C) had principal values 2.0186, 2.0055, and 1.9909. After a few hours at 77 K, B had disappeared completely, A had diminished considerably, and C had increased in intensity. When these experiments were repeated with $Ni(CO)_4$ enriched in the isotope ^{61}Ni ($I = {}^3/_2$), all six transitions revealed hyperfine structure characteristic of two equivalent ^{61}Ni nuclei (e.g. Figure 1). It would appear, therefore, that three distinct binuclear species have been generated.

Table I. Spectral Parameters of Species A, B, and C in Krypton at 77 K

species	parameter	*x*	*y*	*z*
A	*g*		2.1425	
	Ni(2)[a]		−15.4	
	C(2)		31.6	
	C(2 or 4)		9.9	
	C(4 or 2)		11.5	
B	*g*	2.0000	2.0000	1.9781
	Ni(2)[a]	−43.9	−43.9	−42.6
	C(1)	?	?	17.8
	C(6?)	?	?	~3
C	*g*	2.0186	2.0055	1.9909
	Ni(2)[a]	∓6.4	∓5.0	±20.3
	C(2)	10.2	8	9.2
	C(4)	5.1	5	1.0

[a] Two ^{61}Ni nuclei have the given hyperfine interaction (gauss). Sign choices for the ^{61}Ni hyperfine components reflect the fact that the magnetic moment of ^{61}Ni is negative.

The results of ^{13}C enrichment experiments will be presented for each species in turn:

In low enrichment (10–15%) the transition at 2.1425 belonging to A was accompanied by three pairs of satellites, indicative of ^{13}C hyperfine interactions of 31.6, 11.5, and 9.9 G. With very high (99%) ^{13}C enrichment the line at 2.1425 was replaced by a wide (over 100 G) manifold of lines approximately 10.5 G apart. A satisfactory simulation of this spectrum was achieved on the assumptions that (a) 2.1425 is a principal *g* value of an orthorhombic tensor, and not the "perpendicular" value of an axial tensor, (b) two ^{13}C nuclei have 31.6-G hyperfine interactions, and (c) two ^{13}C nuclei have 11.5-G hyperfine interactions, and four have 9.9-G interactions, or vice versa.

The spectrum of species B when enriched in ^{13}C revealed the presence of a unique carbon atom whose hyperfine interaction was 17.8 G at $g = 1.9781$. There was also an indication of small (ca. 3 G) hyperfine interactions with several other carbon nuclei, although the precise number of these could not be determined.

[†] NRCC No. 24884.

(1) Lionel, T.; Morton, J. R.; Preston, K. F. *Inorg. Chem.* **1983**, *22*, 145.
(2) Fairhurst, S. A.; Morton, J. R.; Preston, K. F. *Organometallics* **1983**, *2*, 1869.
(3) Krusic, P. J.; San Filippo, J.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129.
(4) Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131.
(5) Lefebvre, R.; Maruani, J. *J. Chem. Phys.* **1965**, *42*, 1480.
(6) Belford, R. L.; Nilges, M. J. "Computer Simulation of Powder Spectra", EPR Symposium, 21st Rocky Mountain Conference, Denver, CO, Aug 1979.

0020-1669/85/1324-3317$01.50/0 Published 1985 by the American Chemical Society

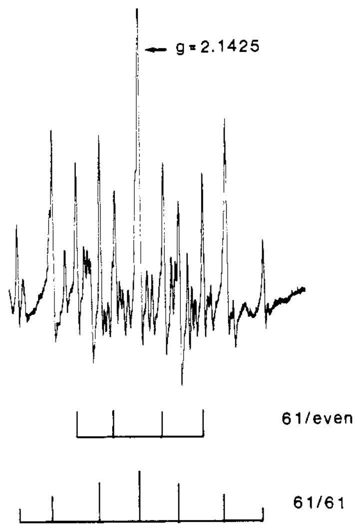


Figure 1. EPR spectrum of species A obtained from a sample containing $Ni(CO)_4$ enriched to 86% in ^{61}Ni. The stick spectra indicate the positions of the allowed transitions of singly and doubly enriched species.

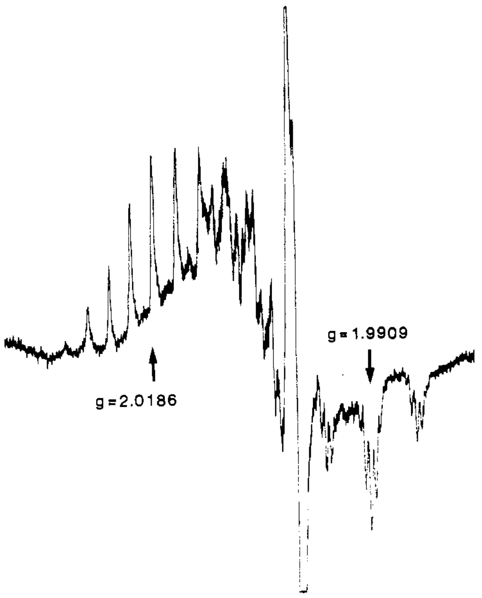


Figure 2. EPR spectrum of species C obtained from a sample containing $Ni(CO)_4$ enriched to 99% in ^{13}C.

The hyperfine structure of the line at $g = 2.0000$ could not be determined because of the complexity of the spectrum in this region.

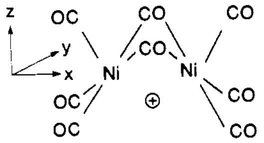
The spectrum of species C was particularly informative after ^{13}C enrichment. The transition at 1.9909 split into three groups (Figure 2) of relative intensities 1:2:1, each group being a 1:4:6:4:1 quintet. ^{13}C enrichment transformed the line at $g = 2.0186$ into a nine-line manifold (Figure 2), which was attributed to interactions with two ^{13}C nuclei at 10.2 G, plus four at 5.1 G. This combination generates a nonet of relative intensities 1:4:8:12:14:12:8:4:1, in excellent agreement with the experimental spectrum. At $g = 2.0055$, the ^{13}C hyperfine structure was difficult to analyze because of overlapping with the adjacent manifold centered at 2.0186, and the line from the Suprasil tube itself. Nevertheless, approximate values of the ^{13}C hyperfine interactions associated with that g value were obtained.

The principal g factors and corresponding ^{61}Ni and ^{13}C hyperfine data for species A, B, and C are assembled in Table I.

Discussion

1. Identification of Species. The three nickel carbonyls that we have observed are unquestionably electronic doublets and are, therefore, charged. We are inclined to believe that A and C are radical cations, although we lack absolute proof. The neutral carbonyls have a formal electronic configuration of $3d^{10}$ at each Ni, so that electron addition would produce radicals having Ni 4s and/or 4p character. Such species would exhibit small ^{61}Ni hyperfine anisotropy and small, negative g shifts from the free-spin value. While it may be argued (see below) that such is the case for radical B, the parameters for A and C are indicative of d-electron-hole species, i.e. radical cations.

Species A appears to be $Ni_2(CO)_8^+$, although with data for but a single direction in the molecule not a great deal more can be said. We postulate for A the bridged structure (C_{2v} symmetry) shown, in which the putative observing direction y is perpendicular to the xz symmetry plane:



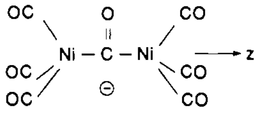
The rationale for this choice is as follows:

(a) Two ligands are clearly distinct from the other six, having ^{13}C hyperfine interactions of 31.6 G. We identify these as the carbon atoms of the bridging ligands. In the hydride-bridged dimer $HFe_2(CO)_8$ we note that the bridging proton had a suprisingly large hyperfine interaction of 22.2 G.[4]

(b) The six terminal ligands have similiar hyperfine interactions, but C_{2v} symmetry permits a distinction between the group of four and the group of two.

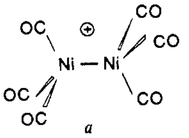
(c) Similar structures have been established for $Co_2(CO)_8$,[7] $HFe_2(CO)_8^-$,[8] and $HCo_2(CO)_8$.[2] In the last radical, the six terminal CO ligands were equivalent for the sole canonical direction that was detected. Considerable unpaired spin density was located on the bridging ligands.

For species B we are obliged to postulate a single bridging carbonyl ligand, with a hyperfine interaction of 17.8 G along z. We know this carbonyl is bridging, since if it were terminal, the two nickel nuclei would not be equivalent. Even so, there is some difficulty in reconciling such a structure with a spectrum having axial symmetry. Our proposed structure is

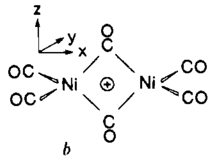


There is, of course, always the possibility of a third principal g factor which we have been unable to locate. But if the spectrum is indeed that of an axial species, its axiality must be due to a hindered motion of the bridging carbonyl ligand about the Ni···Ni direction. Doubtless the terminal ligands would be involved too, which would explain the poor resolution of their hyperfine interactions.

There can be little doubt that species C is the cation radical $Ni_2(CO)_6^+$. The lack of axial symmetry precludes the staggered (D_{3d}) or eclipsed (D_{3h}) ethane-type structures, which would, moreover, exhibit hyperfine interactions with six equivalent ^{13}C nuclei for H_0 parallel to the Ni–Ni bond. With two carbon atoms of one kind and four of another kind for all three axes, the only logical remaining choices seem to be either the C_{2h} structure (a) or the doubly bridged structure (b). Of these alternatives, we



a



b

are inclined to favor structure b. We can offer no reason why $(OC)_3Ni–Ni(CO)_3$ should not have one of the ethane structures;

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(7) Summer, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

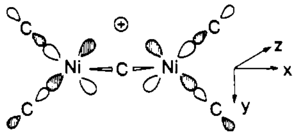
(8) Chin, H. B.; Bau, R. *Inorg. Chem.* **1978**, *17*, 2314.

moreover, the EPR spectrum of structure a would probably be rendered axial by internal motion.

2. Semioccupied Orbitals. With regard to A, little can be said about the spin-population distribution since data are only available for a single direction. The semioccupied molecular orbital (SOMO) of A presumably consits of an antibonding combination of the Ni $3d_{x^2}$ or $3d_{z^2}$ orbitals with no requirement that the resultants lie along the Ni···Ni direction. There may well be a considerable contribution to the SOMO from bridging C 2p orbitals, in view of the large ^{13}C hyperfine interaction from these nuclei.

The key to a correct description of the SOMO for species B lies in the relative signs of the ^{61}Ni tensor components, which are not established. If opposite signs are assumed, the usual method[9] yields an estimated spin population of 0.75 in *each* Ni 3d orbital. The inclusion of spin density on the ligands leads then to an unacceptably high total unpaired spin density. The alternative assumption of all signs the same is only acceptable if the Ni character is essentially 4p: Although we have no estimate for Ni $\langle r^{-3}\rangle_{4p}$, we known its value must be very small. Accordingly, even quite small ^{61}Ni hyperfine anisotropy may imply a substantial unpaired spin population in Ni $4p_z$. It would appear, then, that the anionic formulation $Ni_2(CO)_7^-$ fits the observations best. For the SOMO, we envisage an antibonding combination of two Ni $4p_z$ orbitals and a C $2p_z$ orbital. The observed small negative g shifts are consistent with a single electron in an otherwise empty set of p orbitals.

For species C, we estimate a spin population of 0.23 in each Ni 3d orbital constituent of the SOMO. Considerable spin density must reside on the ligand nuclei, therefore, although the ^{13}C hyperfine data appear to belie this. The observed hyperfine interactions for the group of four carbons may not be principal values, however. Consider the structure and molecular orbital



Cylindrical ^{13}C tensors of (7, −1, −1 G) placed 90° apart at the four terminal positions would be observed as four equivalent nuclei with $|a_{xx}| = 5$ G, $|a_{yy}| = 5$ G, and $|a_{zz}| = 1$ G, exactly as measured (Table I). Such ^{13}C tensors account for as much as 28% unpaired spin density.

The bridging carbons cannot contribute p_x or p_z character directly to this b_{2u} (in D_{2h}) orbital suggested for $Ni_2(CO)_6^+$. They appear to contribute a small amount of s character, and even that may be through polarization. This may account for the anomalously small hyperfine interactions of the bridging ^{13}C nuclei in this species.

Registry No. $Ni_2(CO)_8^+$, 97731-86-7; $Ni_2(CO)_7^-$, 97731-87-8; $Ni_2(CO)_6^+$, 97731-88-9; $Ni(CO)_4$, 13463-39-3.

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(9) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.
(10) Brown, T. L.; Sweany, R. L. *Inorg. Chem.* **1977**, *16*, 415.
(11) Brown, T. L.; Sweany, R. L. *Inorg. Chem.* **1977**, *16*, 421.

Contribution from the Max-Planck-Institut für Festkörperforschung,
7000 Stuttgart 80, Federal Republic of Germany

Metal–Metal Bonding in Transition-Element and Lanthanoid Cluster Compounds. 2

D. W. BULLETT*

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Electronic structure calculations are reported for a number of metal-rich lanthanoid cluster halides, Gd_2Cl_3, Er_4I_5, Er_6I_7, and Er_7I_{10} (and also $NaMo_4O_6$), all of which contain trans-edge-linked (single or double) chains of lanthanoid octahedra, as well as C_2-filled cluster compounds such as $Gd_{10}C_4Cl_{18}$, $Gd_{10}C_4Cl_{17}$, and $Gd_{12}C_6I_{17}$, and the saltlike compound Gd_2NCl_3. The origin of the chemical bonding is analyzed, with particular reference to the extent of metal–metal bonding in each case. The semiconducting gap $E_g \sim 0.7$ eV calculated for Gd_2Cl_3 arises because three d-like states per Gd_4Cl_6 unit are pulled down in energy below the other d states, and these three states may be loosely interpreted as the σ and π states of the strong Gd–Gd bond shared between neighboring octahedra.

In a recent paper[1] electronic structure investigations were reported for a number of metal-rich halides of transition elements and rare-earth metals with particular regard to their metal–metal bonding content. The simplest example considered was NbI_4, in which the metal–metal bonds linking alternate Nb atoms could be clearly identified. The geometrical arrangement of atoms in NbI_4 is such that one of the metal d subbands (consisting primarily of the paired d_{z^2} bonding orbitals directed along the chain direction) is split off below the others, and a clear semiconducting energy gap of about 0.4 eV separates the highest occupied band of metal–metal-bonding states from the lowest unfilled d band. For the double-layer structure of ZrCl a composite group of d bands is pulled down in energy, without a complete energy separation from the higher d bands; the Fermi level E_F falls in a deep, but nonzero, dip in the semimetallic density of states, and no rigorous transformation is possible between the occupied d bands and localized metal–metal-bonding states involving specified d orbitals. It was also shown by a density-of-states calculation that semiconducting behavior would occur in the rather complicated Gd_2Cl_3 structure, although the origin of the calculated (and experimentally observed) 0.7-eV energy gap between occupied and empty states in this material was not clear. In the present submission we begin by analyzing the Gd_2Cl_3 band structure in more detail, to identify the origin of the semiconducting energy gap and to compare the Gd_2Cl_3 bands with those of the closely related $NaMo_4O_6$ structure. We also report calculations of the electronic structure in a number of other metal-rich rare-earth-metal halides, assessing the extent of metal–metal bonding in each case: Er_4I_5, Er_7I_{10}, $Gd_{10}C_4Cl_{18}$, $Gd_{10}C_4Cl_{17}$, $Gd_{12}C_6I_{17}$, and the saltlike Gd_2NCl_3. All the computations follow the method defined earlier,[1] using a basis set of numerical orbitals calculated for neutral atoms—the s, p, and d valence-level orbitals on metal (M) sites, and valence s and p atomic orbitals on ligand (X) sites (as well as Na or C positions where applicable). All matrix elements are calculated by direct numerical integration in the two-center approximation; there are no empirical parameters in this approach. The crystal potential is constructed by overlapping the neutral-atom charge densities of the constituents, with a local-density

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* Address corresondence to the School of Physics, University of Bath, Bath BA2 7AY, England.

(1) D. W. Bullett, *Inorg. Chem.*, **19**, 1780 (1980). A more complete account of the computational procedure used to derive these results may be found in D. W. Bullett, *Solid State Phys.*, **35**, 129 (1980).