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ESR INVESTIGATION OF PARAMAGNETIC CARBONYL-METAL CLUSTERS OF HIGH NUCLEARITY

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Summary

An ESR study has been made of the high nuclearity paramagnetic metal cluster anions $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$, $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$ and $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^-$. The assignment of the HOMO is based on a mixed valence model which relates the g tensor components of cluster systems to those of an appropriate conventional paramagnetic center. With this model the HOMOs of $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$ and of $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$ are found to be mainly comprised of metal d_{z^2} atomic orbitals, while for $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^-$ a large overlap between d atomic orbitals and ligand orbitals is suggested. The occupation of the valence molecular orbitals deduced from the ESR data is consistent with the variations in M—M bond distance observed by X-ray analysis.

ESR studies are increasingly used in investigating the electronic configurations of paramagnetic carbonyl metal clusters [1]. Though most of them are diamagnetic, paramagnetic species are frequently obtained by oxoreductive methods, so that the electronic properties of the paramagnetic derivative and of its diamagnetic parent compound can be compared. The ESR studies con-

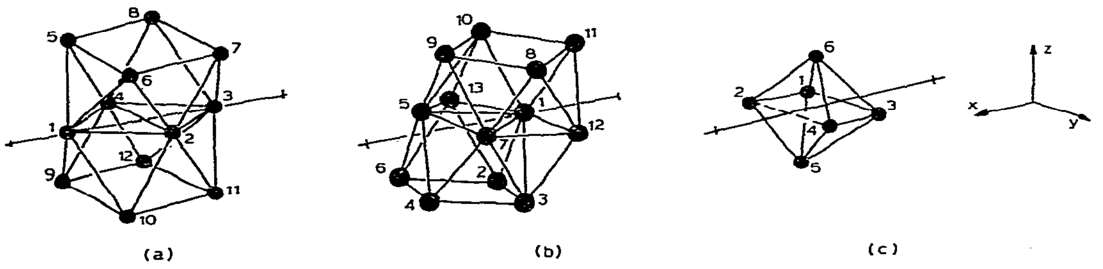

Fig. 1. Metal arrangements of metals in clusters. (a) $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$. (b) $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$. (c) $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]$.

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cerned with the assignment of the HOMO are few and restricted to clusters with low nuclearity [2—4]. The purpose of this paper is to consider the possibility that the electronic configurations of paramagnetic high nuclearity clusters can be discussed on the basis of ESR data. The examples chosen are three paramagnetic carbonyl clusters $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$, $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$, $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^{-}$, whose molecular structures are known from X-ray analysis [5—7]. The metal arrangements are shown in Fig. 1.

Experimental

The tetrapropylammonium salt of $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$, benzyltrimethylammonium salt of $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$ and tetraphenylphosphonium salt of $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^{-}$ were synthesized as reported in refs. 5—7.

ESR measurements were performed on a Varian E 109 spectrometer, equipped with a Varian temperature control in the range 298—77 K, and with an Oxford ESR 900-A continuous flow cooling system, operating in the range 4.2—300 K, continuously adjustable.

ESR results

The tetrapropylammonium salt of $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$, in the polycrystalline phase, was investigated by ESR spectroscopy at temperatures ranging from 4.2 to 298 K.

The spectra indicate an $S = 1/2$ spin state; three well separated g values are visible at temperatures lower than 180 K, while the hyperfine coupling with Rh nuclei cannot be detected. Increase of temperature causes broadening of lines, so that at 298 K only two values of the g tensor components are observed (Fig. 2). The principal values of the g tensor components are in Table 1; derivation of these quantities was assisted by spectral simulation performed by a modified version of SIM 14A program [18].

The spectra of solutions in organic solvents are symmetrical at room temperature, while those of frozen solutions are not substantially different from the powder spectra. Hyperfine coupling with the Rh nuclei is not observed. The g

TABLE 1

ESR PARAMETERS FOR CLUSTER COMPOUNDS [a]

Compound	g_1	g_2	g_3	g_{iso}	T (°K)
$[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$	2.282	2.198	2.038		120 [b,c]—4.2 [b]
				2.155	RT [c]
$[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$	2.183	2.031			4.2 [b]
				2.134	120 [b]
				2.106	120 [c]
$[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^{-}$	2.023	1.975			4.2 [b]
				2.025	120 [c]

[a] The simulation was performed using the values derived from the spectra recorded at 4.2 K. [b] Polycrystalline powder. [c] Organic solvent solution.

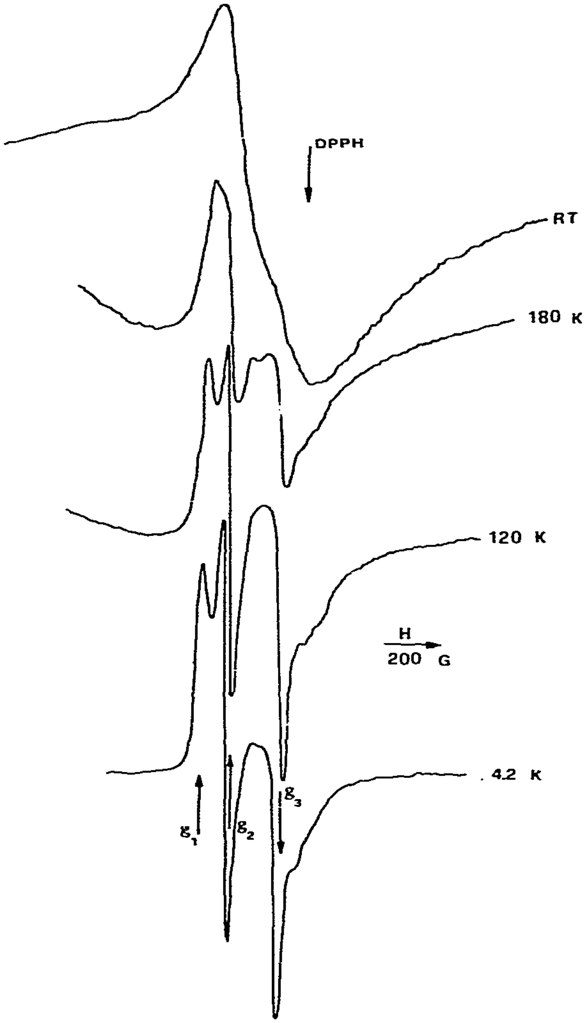


Fig. 2. Temperature dependence of the ESR spectrum of the polycrystalline phase of the tetrapropylammonium salt of $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$.

tensor components are very different from the free electron value, and so it seems that there is high contribution from the spin-orbit coupling of Rh atoms and that the unpaired electron interacts with them.

The benzyl-trimethylammonium salt of $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$ does not give an ESR spectrum at 298 K, either in the solid state or in solution in organic solvents. Both the powder and the frozen solutions at 120 K show a symmetrical strong absorption line, indicative of $S = 1/2$ spin state. At 4.2 K the anisotropy of g tensor becomes evident in the powder spectrum, and the best fit reveals axial symmetry of the g tensor. However a small degree of rhombic distortion cannot be excluded because of the large line width.

The displacement of g values from the free electron value suggests that the unpaired electron is located mainly on the cobalt atoms. Hyperfine coupling with the Co nuclei is not observed (Fig. 3a).

The tetraphenylphosphonium salt of $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^-$ gives a sym-

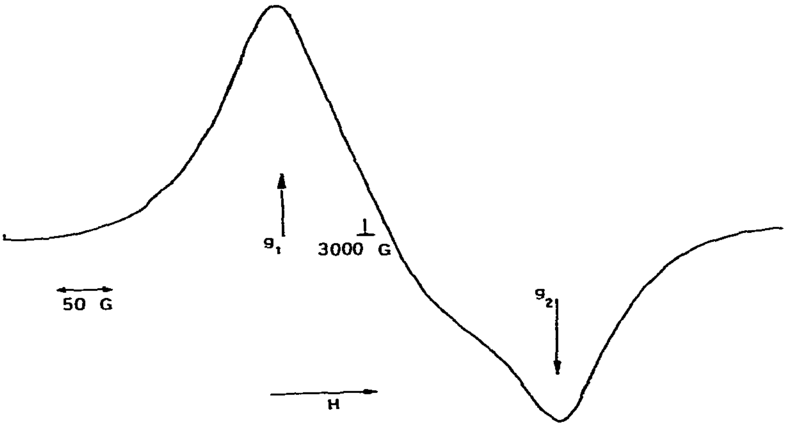


Fig. 3a. ESR spectrum of the polycrystalline phase of the benzyltrimethylammonium salt of $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$, recorded at 4.2 K.

metrical signal in solution and in solid state in the range 298—120 K. At 4.2 K the anisotropy of *g* tensor becomes evident and two components can be observed. The spectrum is indicative of an $S = 1/2$ spin state and hyperfine coupling with cobalt is not observed. (Fig. 3b.)

All the results of ESR investigation are collected in Table 1.

Electronic structure and bonding

The main problem is how to deduce the ground state configurations of the clusters from the ESR data. The results of ESR investigation, when used alongside the data from electronic spectroscopy very satisfactorily define the ground state configurations of paramagnetic mono-metal coordination compounds.

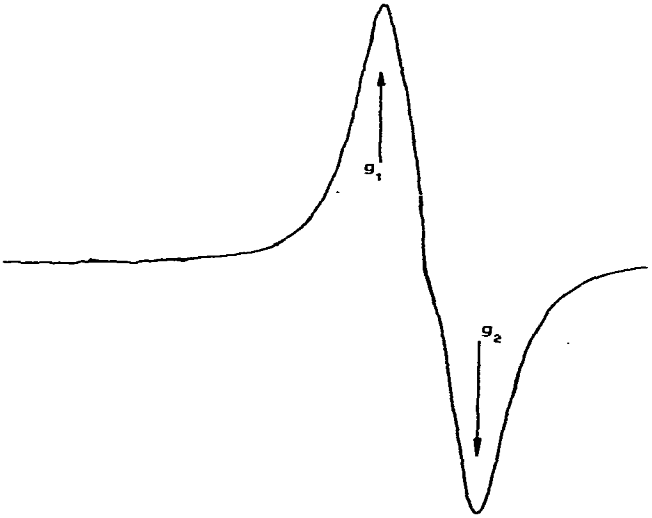
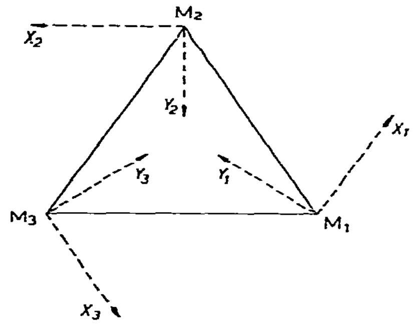


Fig. 3b. ESR spectrum of the polycrystalline phase of the tetraphenylphosphonium salt of $[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^-$ recorded at 4.2 K.

However, for metal cluster systems the available information on electronic energy data is generally not enough to define the magnetic tensor components as a function of the ground state configuration. Longuet-Higgins and Stone [2] first attempted to use a modified crystal field approach to calculate the g tensor components of [$Ni_3(CO)_2(Cp)_3$], but their assignment of the ground state configuration was ambiguous because they needed much more electronic data than they had, and their conclusions were later shown to be wrong [3].

The ESR properties of [$Fe_3Pt_3(CO)_{15}$]$^-$, a paramagnetic carbonyl cluster obtained by mild oxidation of [$Fe_3Pt_3(CO)_{15}$]$^{2-}$, give us the chance to reconsider the general problem of assigning the ground state configuration in paramagnetic metal clusters from ESR data [4]. The ESR parameters of [$Fe_3Pt_3(CO)_{15}$]$^-$ suggested that the unpaired electron lies mainly in the Pt_3 molecular orbitals, delocalized over the three Pt centers. If we think of the compound as [$Pt_3(\mu_2$-$Fe(CO)_4)_3(CO)_3$]$^-$, and, following Dahl's approximation [3], we separate the metal—ligand from the metal—metal interactions, we conclude that suitable combinations of three valence orbitals of each Pt (namely $6s$, $6p_x$, $6p_y$) are involved in bonding with ligands; the remaining 25 electrons are located in the fifteen molecular orbitals obtained by combination of atomic d orbitals of Pt, with D_{3h} symmetry. By ordering the energy of these MO on the overlap basis, the unpaired electron can be located in the $(a_2')^*$ MO which can be formulated as $1/\sqrt{3}\,(d_{xy_1} + d_{xy_2} + d_{xy_3})$ (1, 2, 3 indicate the Pt atoms of Scheme 1).



SCHEME 1

The larger Pt—Pt bond distance found in [$Fe_3Pt_3(CO)_{15}$]$^{2-}$ (26 electrons) with respect to [$Fe_3Pt_3(CO)_{15}$]$^-$ (25 electrons) confirmed the antibonding nature of the HOMO, with electron density maxima along the Pt—Pt bond directions.

In order to reproduce the g tensor components by the method proposed by Longuet-Higgins and Stone [2], it is necessary to fit the expressions

$$g_{/\!/} = 2 + 8\zeta/E(\phi_2) - E(\phi_1)$$

$$g_{\perp} = 2 + \zeta/E(\phi_3) - E(\phi_1) + \zeta/E(\phi_4) - E(\phi_1)$$

$$\phi_1 = 1/\sqrt{3}\,(xy_1 + xy_2 + xy_3)$$

$$\phi_2 = 1/\sqrt{3}\,((x^2 - y^2)_1 + (x^2 - y^2)_2 + (x^2 - y^2)_3)$$

$$\phi_3 = 1/\sqrt{3}\,(xz_1 + xz_2 + xz_3)$$

TABLE 2

CORRELATION BETWEEN ESR PARAMETERS AND ELECTRONIC CONFIGURATION IN CLUSTERS AND IN MONONUCLEAR MODEL COMPOUNDS

Cluster compound	Ref.	g_{zz}	g_{xx}	g_{yy}	N.E.[a]	Formal metal configuration	HOMO in cluster
$[Fe_3Pt_3(CO)_{15}]^-$	4	2,57	2,03		25	$1Pt(d^9)\ 2Pt(d^8)$	$1/\sqrt{3}\ (d_{xy_1} + d_{xy_2} + d_{xy_3})$
$[Co_3(CO)_9S]$	3	2,04	2,02		25	$1Co(d^9)\ 2Co(d^8)$	$1/\sqrt{3}\ (d_{xy_1} + d_{xy_2} + d_{xy_3})$
$[(C_5H_5)_3Ni_3(CO)_2]$	2	2,11	2,02		19	$1Ni(d^7)\ 2Ni(d^6)$	$1/\sqrt{3}\ (d_{xy_1} + d_{xy_2} + d_{xy_3})$
$[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$		2,038	2,198 or 2,282	2,282 or 2,198	83	$11Rh(d^7)\ 1Rh(d^6)$	$\Sigma_i(a_i d_{z_i^2} + b_i d_{xy_i})$
$[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$		2,031	2,183		89	$11Co(d^7)\ 2Co(d^6)$	$\Sigma_i(a'_i d_{z_i^2} + b'_i d_{xy_i})$
$[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^-$		2,023 or 1,975	1,975 or 2,023		39	$3Co(d^7)\ 3Co(d^6)$	undetermined

Model compound	Ref.	g_{zz}	g_{xx}	g_{yy}	Electron configuration	Ground state
$[PtCl_3]^{2-}$	9	2,800	2,174	1,974	d^9	$d_{x^2-y^2}$
$[Co(CO)_4]$ (Ar matrix)	10	2,132	2,012		d^9	$d_{x^2-y^2}$
$[Co(CO)_4]$ (CO matrix)	10	2,007	2,128		d^9	d_{z^2}
$[Ni(12\ aneN_4)]^{3+}$	11	2,17	2,06		d^7	$d_{x^2-y^2}$
$[Ni(13\ aneN_4)]^{3+}$	11	2,02	2,20		d^7	d_{z^2}
Rh(II)AgBr (35°K)	12	2,03	2,359		d^7	d_{z^2}
Rh(II)AgBr (100—200°K)	12	2,37	2,19		d^7	$d_{x^2-y^2}$
$[Co(Pc)Py_2]$	13	2,01	2,20		d^7	d_{z^2}

[a] N.E. = number of electrons available to M—M bonds.

$\phi_4 = 1/\sqrt{3}\,(yz_1 + yz_2 + yz_3)$

ζ = spin orbit coupling constant.

For this, more experimental data would be needed than we have available. This argument shows that the fitting of experimental g values is impossible, and thus that the nature of HOMO cannot be inferred by this method.

On the other hand we observe that the g tensor components of the mentioned cluster show a trend similar to that of $[PtCl_3]^{2-}$ (provided that the $g_\perp$ value of the cluster is compared with the mean value of g_{xx} and g_{yy} of $[PtCl_3]^{2-}$), a mononuclear compound with d^9 Pt configuration, where the unpaired electron is located in the in plane $d_{x^2-y^2}$ orbital [9]. It seems to us that the similarity between the g tensor components of $[Fe_3Pt_3(CO)_{15}]^-$ and of $[PtCl_3]^{2-}$ is not coincidental, but reflects a correspondence between the respective ground states; $[PtCl_3]^{2-}$ has the unpaired electron located in the $d_{x^2-y^2}$ orbital, while $[Fe_3Pt_3(CO)_{15}]^-$ has the unpaired electron located in a linear combination of the three Pt d_{xy} orbitals. (In D_{3h} symmetry d_{xy} and $d_{x^2-y^2}$ orbitals are degenerate.) Hence we suggest that, if the values of the g magnetic tensor of a cluster compound suggest that the unpaired electron lies in an MO mainly comprised of atomic d orbitals, then:

(1) The number of electrons available to the metal—metal bond can be calculated using Dahl's approximation, which separates metal—ligand from metal—metal interactions.

(2) These electrons can be divided among the metal atoms of the cluster so that either one center results in an odd-electron configuration and the others in diamagnetic configurations, or the number of formal paramagnetic centers is odd, but an even number of them are perfectly paired by direct bond interactions.

(3) The whole molecular system is then formally represented by the paramagnetic center derived from argument 2. Experimental g values for the cluster are compared with those of mononuclear compounds of the same metal in the same d electron configuration. If agreement is found between the trends in the respective g components, we suggest that the HOMO in the cluster is mainly comprised of the same type of atomic orbital as the ground state in the model mononuclear compound.

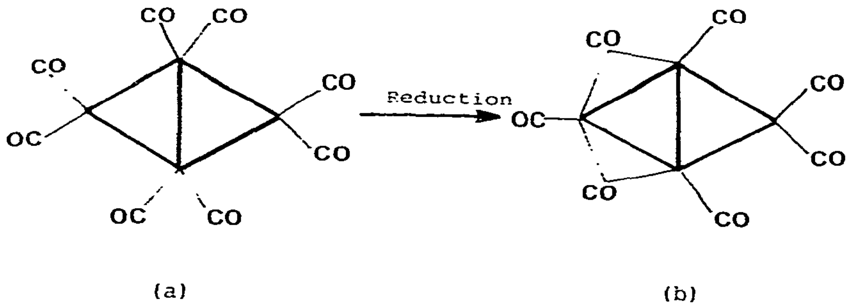
The proposed correlation scheme has been successfully applied to the paramagnetic trinuclear carbonyl metal clusters as shown in Table 2. It is noteworthy that, with this model the HOMO of $[Ni_3(CO)_2(Cp)_3]$ would not have been erroneously [2] suggested to be comprised of atomic orbitals out of the Ni_3 plane; the sequence $g_{/\!/} > g_\perp > 2$ rules out for the model d^7 configuration location of the unpaired electron out of the molecular plane. The procedure described above is used below in order to give insight into the nature of the HOMO of the three high nuclearity clusters now under consideration.

$[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$

The X-ray structure [5] of this cluster suggests that 83 electrons are available to the metal—metal bonds, being 8 of the 108 rhodium electrons involved in the rhodium—carbide σ bonds and 20 in the rhodium—bridging carbonyl σ bonds. A symmetric distribution of the 83 electrons over 12 Rh atoms gives an electronic configuration near the d^7 configuration. Since the eight Rh atoms forming the base of the polyhedron (n. 5, 6, 7, 8, 9, 10, 11, 12 of Fig. 1a) must be chemically equivalent as they are derived from two equivalent Rh_6C polyhedra, an identical d^7 configuration can be proposed for them, for a total number of 56 implied electrons. The remaining 27 electrons can be distributed over the rhodium atoms in the intermediate plane (n. 1, 2, 3, 4 in the Fig. 1a), as three Rh formally d^7 and one Rh d^6. In this plane two of the four atoms are equivalent by symmetry and paired by direct bonding, the others being unique because they lie on the C_2 axis. Thus the whole cluster can be regarded in terms of its magnetic properties as a rhodium(II) d^7 system.

Spectral changes with temperature (Fig. 2) suggest that g_1 and g_2 are probably components of $g_\perp$, so that the order of g values is $g_\perp > g_{//}$. If we compare the g component sequence for the cluster with that of the rhodium(II) mononuclear compounds, shown in Table 2, the ground state of $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$ is seen to involve a molecular orbital mainly comprised of d_{z^2} orbitals. We suggest that there is also mixing with the molecular orbital mainly comprised of d_{xy} orbitals (allowed in C_{2v} symmetry), in order to explain the sequence $g_3 > g_e$.

The assignment of the HOMO cannot be deduced from the sequence of energies of the molecular symmetry orbitals, as it was done for $[Fe_3Pt_3(CO)_{15}]^-$: overlap arguments are difficult to use in systems of such a complexity. However assuming that the reduction [5] of diamagnetic $[Rh_{12}(CO)_{16}(\mu_2\text{-}CO)_8(C)_2]^{2-}$ to the paramagnetic $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$ mainly perturbs the equatorial plane of the Rh_{12} skeleton (Scheme 2), we suggest that the HOMO is mainly comprised of d atomic orbitals of the Rh atoms in this plane.



SCHEME 2. Bonding geometry of equatorial plane in (a) $[Rh_{12}(CO)_{16}(\mu_2\text{-}CO)_8(C)_2]^{2-}$, (b) $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$.

$[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$

The number of electrons available to metal—metal bonds is 89, close to 7 for each Co atom in a symmetrical distribution over those atoms. Again 8 cobalt atoms can be considered chemically equivalent (n. 2, 3, 4, 6, 8, 9, 10, 11 of Fig. 1b), as they are derived from two identical Co_6C units. A d^7 configuration involves 56 valence electrons for these atoms; the remaining 33 electrons can be formally distributed in the plane of the five atoms (n. 1, 5, 7, 12, 13 in Fig. 1b), as 3 Co d^7 and 2 Co d^6. In this plane one cobalt is unique, lying on the C_2 axis, while the others are paired by symmetry and bonding. A d^7 configuration is suggested for the center which formally represents the magnetism of the whole cluster. Examples of mononuclear d^7 cobalt compounds are common; and if we assign g_1 to $g_\perp$ and g_2 to $g_{//}$, as from the spectral simulation, the g component trend of the cluster is in agreement with that proposed for d^7 cobalt compounds having the unpaired electron in the d_{z^2} orbital. Thus the HOMO is seen to be mainly comprised of d_{z^2} atomic orbitals. The relationship $g_{//} > 2$ indicates a mixing with d_{xy} orbitals.

If we consider that the Co(1)—Co(7) and Co(1)—Co(5) bonds are significantly longer than all the other metal—metal bonds [6], the HOMO of this cluster must be mainly comprised of d orbitals of the cobalts in the Co(1)—Co(7)—Co(5) plane.

$[Co_6(CO)_8(\mu_2\text{-}CO)_6C]^-$

The electrons available to Co—Co bonds are 39, 6.5 for each of the metal centres. They can be distributed between 3 Co d^7 and 3 Co d^6 centres. Thus the formally paramagnetic centre once again has the d^7 electronic configuration. Unfortunately the shape of ESR line does not allow any assignment of g tensor components, and all hypotheses about the ground state configuration could be wrong. Moreover the g tensor values of the cluster suggest that if the formal paramagnetic centre has d^7 electronic configuration, the unpaired electron must be largely delocalized over the ligands, and so all proposals based on the crystal field approach could be in error. The anomalously long Co(2)—Co(4) bond, revealed by the X-ray studies [7], may be the only proof of the involvement of d_{xy} orbitals of the Co atoms lying in the xy plane (see Fig. 1c).

Concluding remarks

The results presented show that the nature of the HOMO can be deduced by comparison of the magnetic properties of the whole cluster with those of an appropriate conventional metal center. The HOMO's proposed for high nuclearity systems confirm the feature observed in the low (three) nuclearity systems [3,4], namely that the presence of the unpaired electron can have a considerable influence on the metal—metal bond lengths as a function of the directionality of the valence orbitals. The distribution of the unpaired electron in the clusters is consistent with the chemical differences among the metal atoms; thus the inhomogeneous distribution of the unpaired electron, proposed for $[Rh_{12}(CO)_{13}(\mu_2\text{-}CO)_{10}(C)_2]^{3-}$ and $[Co_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}(C)_2]^{4-}$, is in agreement with the chemical uniqueness of the rhodium or cobalt atoms in the equatorial plane and also with the alternating charge noted in other stratified clusters of this type [14].

Acknowledgment

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References

1 B.M. Peake, P.H. Rieger, B.H. Robinson and J. Simpson, Inorg. Chem., 20 (1981) 2540.
2 H.C. Longuet-Higgins and A. Stone, Mol. Phys., 5 (1962) 417.

3 C.E. Strouse and L.F. Dahl, Discuss. Farad. Soc., (1969) 93.
4 G. Longoni and F. Morazzoni, J. Chem. Soc. Dalton, (1981) 1735.
5 V.G. Albano, D. Braga, S. Martinengo and D. Strumolo, Atti del XIV Congresso della Società Chimica Italiana, Catania (1981) 275.
6 V.G. Albano, D. Braga, P. Chini, G. Ciani and S. Martinengo, J. Chem. Soc. Dalton, in press.
7 V.G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. Heaton and S. Martinengo, J. Am. Chem. Soc., 98 (1976) 5027.
8 G.P. Lozos, B.M. Hoffman and C.G. Franz, Quantum Chemistry Program Exchange, N. 265 (1974).
9 T. Krigas and M.T. Rogers, J. Chem. Phys., 55 (1971) 3035.
10 L.A. Hanlan, H. Huber, E.P. Kundig, B.R. McGarvey and G.A. Ozin, J. Am. Chem. Soc., 97 (1975) 7054.
11 A. Bencini, L. Fabbrizzi and A. Poggi, Inorg. Chem., 20 (1981) 2544.
12 R.S. Eachus and R.E. Graves, J. Chem. Phys., 61 (1974) 2860.
13 F. Cariati, D. Galizzioli, F. Morazzoni and C. Busetto, J. Chem. Soc. Dalton, (1975) 556.
14 B. Heaton, C. Brown, D.O. Smith, L. Strona, R.J. Goodfellow, P. Chini and S. Martinengo, J. Am. Chem. Soc., 102 (1980) 6175.