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# On the Electronic Structure of the $Ni_2^{4+}$ Ion and Its Relation to the Metal–Metal Bonding in Binuclear Ni(II) Complexes

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In an attempt to improve the understanding of the electronic structure of the $Ni^{2+}$ thiocarboxylates, we have analized, as a zeroth-order approximation, the electronic structure of the $Ni_2^{4+}$ dimer *in vacuo*. Two small-size Slater-type orbitals (STO) basis sets have been used in order to study basis effects, referring particularly to the details of the *d–d* interactions. All electrons have been included and all the molecular integrals have been computed accurately. All the multiplets of the $\{Ar_2\}\sigma_g^2\sigma_u^2\pi_g^4\pi_u^4\delta_g^x\delta_u^{4-x}$ ($x$ = 0 to 4) configurations have been calculated at different values of the $Ni^{2+}$–$Ni^{2+}$ distance, $R$, ranging from 3.20 to 5.20 a.u. in the smaller basis calculation and from 3.20 to 4.20 a.u. in the larger basis calculation. Inclusion of configuration interaction (CI) limited to the $\delta_g^x\sigma_u^{4-x}$ ($x$ = 0 to 4) configurations yields a $^3\Sigma_g^-$ as the lowest multiplet. This CI reduces $R_e$ from 2.03 to 1.76 Å, an effect also encountered in much more extensive CI calculations on $Ni_2$. The bonding in $Ni_2^{4+}$ is discussed in terms of the $R$ dependence of the orbital energies; $\sigma$, $\pi$, and $\delta$ interactions seem to make important contributions to the bonding, in view of their orbital splittings and stabilizations with respect to the free-ion values. The present results are compared with previous nonempirical studies on the $Ni_2$ and $Ni_2^+$, as well as with empirical relationships among different molecular constants. The relevance of the results on $Ni_2^{4+}$ to the question of the metal–metal interaction in $\{Ni(R\text{–}COS)_2\}_2$ compounds is difficult to discuss with certainty, but, mainly from the theoretical geometry obtained, it is argued that the $Ni^{2+}$–$Ni^{2+}$ interactions might have a very small contribution to the selling of the electronic structure of the thiocarboxylates. © 1985 Academic Press, Inc.

## I. Introduction

In this paper we report our results on the calculation of the electronic structure of the $Ni_2^{4+}$ ion. This work was conceived as a convenient step in the understanding of the metal–metal interaction in the more complicated electronic structure of the $Ni^{2+}$ thiocarboxylates with bridging cage structures. The importance of such interaction in this type of compounds was suggested by Bonamico *et al.* (*1*), who determined the crystal structure of the $Ni^{2+}$ monothiobenzoate and the $Ni^{2+}$ dithiopheylacetate, and found internuclear nickel–nickel distances of 4.71 and 4.84 a.u., respectively. These authors argued that such short distances should be due to the operation of a metal–metal bond. Further support to this hypothesis was given by Taylor (*2*), who explained some irregularities in the magnetic behavior of several binuclear $Ni^{2+}$ complexes in terms of a metal–metal interaction. On the other hand, Melson *et al.* (*3, 4*), based on crystallographic, spectroscopic, and magnetic evidences, proposed that in this type of complex dimers the electronic structure of the $Ni^{2+}$ ions is determined by their inter-

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actions with the neighbor oxygen and sulfur atoms rather than by the nickel–nickel interaction. We have recently analyzed this question (*5, 6*), interms of crystal-field calculations, and have found that the optical spectra and the magnetic character of these complex dimers are best interpreted if the nickel–nickel interaction is neglected.

The present work is a continuation of our previous analysis (*6*). Instead of focusing the attention into the nickel–oxygen and nickel–sulfur interactions, we have computed the electronic structure of the isolated $Ni_2^{4+}$ ion in the framework of the restricted Hartree–Fock–Roothaan (HFR) molecular orbital theory. We have not considered an extensive configuration interaction in the calculation but all electrons have been included and all the integrals have been computed accurately. Two STO basis sets have been used in order to explore basis set effects and to have an indication on the plausibility of our predictions. Obtaining approximate information, from HFR theory, on some aspects of the $Ni^{2+}$–$Ni^{2+}$ interaction, useful in understanding the electronic structure of the thiocarboxylates, has been the aim of this work more than to perform a detailed, large-scale calculation of the $Ni_2^{4+}$ electronic structure. We expect that some of the theoretical results reported in this work could be of interest in the study of these thiocarboxylates.

From our calculation we tentatively propose a $^3\Sigma_g^-$ as a possible ground state for the $Ni_2^{4+}$ ion, with $R_e$ = 1.76 Å and $\omega_e$ = 814 $cm^{-1}$. These and other results are discussed in connection with previous nonempirical results on $Ni_2$ and $Ni_2^+$, and with empirical relationships among different spectroscopic constants. We argue that the present calculation supports the idea, advanced by Melson *et al.* (*3, 4*), of a negligible contribution of the metal–metal interaction to the electronic structure and geometry of the $Ni^{2+}$ thiocarboxylates.

## II. Method

Previous work on $Ni_2$ and $Ni_2^+$ (*7–9*), suggests that the ground state of $Ni_2^{4+}$ would belong to one of the $\{Ar_2\}\sigma_g^2\sigma_u^2\pi_g^4\pi_u^4\delta_g^x\delta_u^{4-x}$ ($x$ = 0 to 4) configurations. These configurations, that from now on will be referred to as $\delta_g^x\delta_u^{4-x}$, come from the $\{Ar\}3d^8$ configuration of the $Ni^{2+}$ ion. We have not considered configurations coming from the $\{Ar\}3d^74s$ configuration of the $Ni^{2+}$ ion because its lower multiplet lies 6.7 eV above the ground state (*10, 11*). This situation differs from those in neutral Ni, where the $3d^94s$–$^3D_3$ lies about 0.025 eV above the $3d^84s^2$–$^3F_4$ ground state (*10*) and gives rise to the ground configuration of $Ni_2$ (*8*), and in $Ni^+$, where the $3d^84s$–$^4F$ lies about 1.1 eV above the $3d^94s$–$^2D$ ground state (*10*). These facts suggest that the contribution of the $4s$–$4s$ interactions to the ground state of the nickel dimers would be fairly less important in $Ni_2^{4+}$ than in $Ni_2$ or in $Ni_2^{4+}$.

We have analyzed all the multiplets coming from the $\delta_g^x\delta_u^{4-x}$ ($x$ = 0 to 4) configurations in terms of the self-consistent field (SCF) solutions of the $\delta_g^2\delta_u^2$–$^5\Sigma_g^+$ state. The necessary wavefunctions for these multiplets have been obtained by means of the projector operator technique of Löwdin (*12*).

Our limited computer facilities have forced us to use very small basis sets in the SCF calculation. First, we use a 1-$\zeta$ STO basis fully optimized for the $\{Ar\}3d^8$–$^3F$ ground state of the $Ni^{2+}$ ion. The parameters of this basis are collected in Table I. This basis will be referred to, from now on, as basis I. In order to improve the description of the d–d interactions in $Ni_2^{4+}$, we also have used the approximate HF basis set of Richardson *et al.* (*13*). In this basis the $3d$ atomic orbitals (AO) are written in terms of two STO's. This basis will be referred to as basis II.

We have solved the SCF equations for the $\delta_g^2\delta_u^2$–$^5\Sigma_g^+$ state of the $Ni_2^{4+}$ ion in both bases. Eight different values of $R$, from

TABLE I

STO BASIS SET OPTIMIZED FOR THE $3d^8$–$^3F$ GROUND STATE OF THE $Ni^{2+}$ ION[a]

| $nl$ | $\zeta$ | $1s(-306.187)$ | $2s(-38.0230)$ | $3s(-5.07958)$ | $4s(10.7375)$ |
|---|---|---|---|---|---|
| $1s$ | 27.4401 | 0.997865 | 0.347927 | −0.137411 | −0.321683 |
| $2s$ | 8.79723 | 0.009486 | −1.410479 | 0.662029 | 1.923842 |
| $3s$ | 4.90210 | −0.026211 | 2.051079 | −2.138756 | −13.14958 |
| $4s$ | 5.72600 | 0.022606 | −1.752412 | 0.894630 | 12.30640 |

| $nl$ | $\zeta$ | $2p(-33.2978)$ | $3p(-3.55003)$ |
|---|---|---|---|
| $2p$ | 12.0454 | 0.986017 | 0.355527 |
| $3p$ | 4.69382 | 0.043760 | −1.047241 |

| $nl$ | $\zeta$ | $3d(-0.70171)$ |
|---|---|---|
| $3d$ | 4.17657 | 1.000000 |

Total energy = −1501.6705 a.u.
$\langle V\rangle$ = −3004.8983 a.u.
$\langle T\rangle$ = 1503.2278 a.u.
Virial theorem: −1.99896

$F^0(3d, 3d)$ = 1.078130 a.u.
$F^2(3d, 3d)$ = 0.569111 a.u.
$F^4(3d, 3d)$ = 0.371160 a.u.

[a] Orbital energies (in a.u.) in parentheses.

3.20 to 5.20 a.u., have been considered in calculations with basis I, and four values, from 3.20 to 4.20 a.u., in calculations with basis II.

Configuration interaction limited to the $\delta_g^x\delta_u^{4-x}$ ($x = 0$ to 4) configurations has been considered for the $^3\Sigma_g^-$ (2 × 2) and for the $^1\Sigma_g^+$ (5 × 5) states.

Bases I and II considered in this work include the empty $4s$ AO. In basis II it was obtained by simulating the results of Watson on the $3d^64s^2$ configuration (*13*). The $4s$ orbital exponent in basis II is $\zeta(4s) = 1.50$ (*13*). Values of $\zeta(4s)$ used in calculations on diatomic nickel range from 1.42 to 2.28 (*15*). Our results in the $s$-block of basis I (Table I) show the limitations of optimizing orbital exponents in bases which contain empty orbitals and have low flexibility (small number of basis functions). The value $\zeta(4s) = 5.7260$ obtained in basis I minimizes the total energy of the $3d^8$–$^3F$ state of $Ni^{2+}$ but it is very close to the value of $\zeta(3s)$ and gives rise to a rather contracted $4s$ AO. The high coefficients in the $3s$ and 4s AO's are a consequence of this proximity between $\zeta(3s)$ and $\zeta(4s)$. Furthermore, the compactness of this virtual AO implies (i) a large value of its kinetic energy, (ii) large electron repulsions with the occupied AO's, and (iii) large, in absolute value, nuclear attraction energy. The sum of these effects gives a highly unstable virtual AO, with an orbital energy of +10.7 a.u. This number contrasts with the corresponding in basis II, i.e., $\varepsilon(4s) = -0.55$ a.u.. Thus, the $4s$ AO of basis I is inappropriate to describe states of configurations other than the $3d^8$. In the calculations reported in this paper the $4s$ AO acts as an extra degree of freedom, since we dot not consider states in which this orbital is occupied. We will see in Results and Discussion that, apart from a larger variational efficiency in calculations with basis II, the electronic states of the $Ni_2^{4+}$ dimer show a highly parallel behavior in the two bases, in spite of the large differences in their $4s$ AO. This result indicates the small contribution of the $4s$–$4s$ interactions, by comparison with the $3d$–$3d$ interactions, in the electronic states of $Ni_2^{4+}$ discussed in this work.

## III. Results and Discussion

The results of our diagonal calculation are partly collected in Fig. 1. Only the four lower multiplets are shown. Calculations with basis I and basis II give the same ordering for these states, at this level of approximation. When basis II is used, the total energy of these multiplets is lowered by about 2.2 a.u., but the values of $R_e$ are not greatly modified. The characteristics of these electronic states at their equilibrium positions are presented on Table II, as computed with the two bases. Increasing the basis size, from basis I to basis II, results in an increase of $R_e$ by about 0.05 Å. This change in $R_e$ can be due to the more diffuse $3d$ and $4s$ AO's in basis II, and it is comparable to those changes found by Schmidtke and Wolf (*15*) in their analysis of basis set effects in $Sc_2$ and $Cu_2$. The basis effect on $\omega_e$ are not very large and compare well with those quoted in Ref. (*15*). All other multiplets in Fig. 1 and Table II are quite parallel to the $^5\Sigma_g^+$ state, in both bases. These relatively small basis effects on $R_e$ constitute a particularly interesting result from the point of view of the metal–metal interaction in binuclear $Ni^{2+}$ thiocarboxylates, as we comment below.

TABLE II

EQUILIBRIUM PROPERTIES OF THE FOUR LOWER MULTIPLETS COMPUTED FROM RESULTS OF THE DIAGONAL SCF CALCULATION ON THE $^5\Sigma_g^+$ STATE OF $Ni_2^{4+}$

| State | $E_e$ (a.u.) | $R_e$ (a.u.) | $D_e$ (eV) | $\omega_e$ (cm$^{-1}$) |
|---|---|---|---|---|
| $^5\Sigma_g^+$ | −3001.9276 | 3.73 | −38.46 | 581 |
| | −3004.1225 | 3.84 | −37.64 | 668 |
| $^1M_g$ | −3001.8097 | 3.73 | | 581 |
| | −3004.0331 | 3.84 | | 666 |
| $b\ ^3\Sigma_g^-$ | −3001.8097 | 3.73 | | 581 |
| | −3004.0331 | 3.84 | | 666 |
| $b\ ^1\Sigma_g^+$ | −3001.7607 | 3.73 | | 581 |
| | −3003.9966 | 3.84 | | 676 |

*Note*. First row entries correspond to basis I; second row entries to basis II.

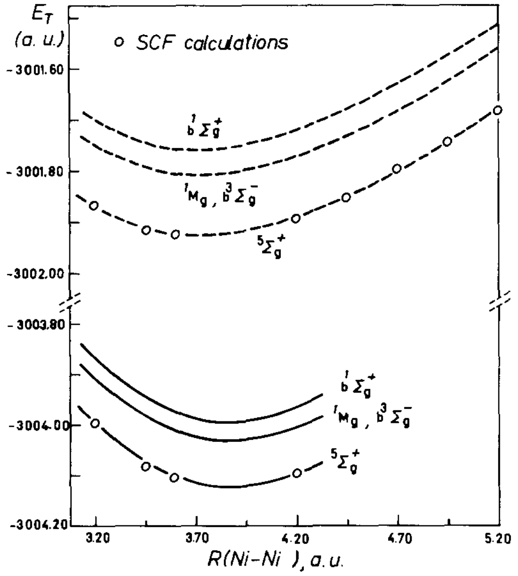

FIG. 1. Diagonal calculation of the lower multiplets of $Ni_2^{4+}$. Basis I (broken lines) and basis II (solid lines) results are shown.

The diagonal calculation gives a negative dissociation energy in both bases, as Table II reveals. Negative dissociation energies have been found in neutral transition-metal dimers, such as $Cr_2$ (*16*), and they have been associated to the correlation error. In $Ni_2^{4+}$, however, it is interesting to recall that the classical, pure electrostatic $Ni^{2+}$–$Ni^{2+}$ repulsion gives a contribution of 29.2 eV at $R = 3.73$ a.u. ($R_e$, basis I), and 28.3 eV at $R = 3.84$ a.u. ($R_e$, basis II). We find, then, that in both cases the classical ionic repulsion represents the 75% of the diagonal dissociation energy. Given the strongly repulsive character of this classical interaction, the presence of minima in our diagonal nuclear potentials can be seen as an indication of strong noncoulombic nickel–nickel interactions at these values of $R$. Furthermore, our diagonal HFR values of $D_e$, about 9 eV higher than the classical contribution, suggest that this calculation could be noticeably improved by (i) extending the size of the basis set, and (ii) dealing with the correlation error. This is adequately confirmed by our CI results, which give dissociation energies positive and dependent on the basis quality (see Table V). An estimate of the $R$ dependence of the noncoulombic energy can be deduced from the numbers in Table IV. The lower $^3\Sigma_g^-$ state shows a decrease in energy of 10.6 eV (basis I), from $R$ = 4.70 to 3.60 a.u., after CI. Since the coulombic repulsion increases by 7.1 eV in this interval, the noncoulombic energy must decrease by 17.7 eV, from $R$ = 4.70 to 3.60 a.u. (i.e., with a gradient of about 30 eV · Å$^{-1}$). This nonclassical interaction should be able to produce a binding situation at about $R$ = 3.7 a.u., according to our results, but its short-range character will make it much smaller, in absolute value, at $R$ = 4.70 a.u., the observed internuclear separation in $Ni^{2+}$ thiocarboxylates. This suggests that at such large distance the metal–metal interaction could be dominated by the classical repulsion.

Further insight on the $Ni^{2+}$–$Ni^{2+}$ interaction can be gained by examining the orbital energies of the MO's formed by the 3$d$ orbitals. Such information is collected in Table III, at several values of $R$, for the two bases. Numbers in Table III correspond to the respective SCF calculation on the $^5\Sigma_g^+$ state. The orbital energies show a smooth reduction when $R$ decreases, with similar slopes for the three symmetries. One of the more interesting results deducible from this table is that both basis sets give practically the same qualitative picture of the metal–metal interaction. In passing from basis I to basis II, the stabilization per electron, at $R$ = 3.60 a.u., turns out to be 12.3 eV for $\sigma$ orbitals in basis I (12.7 eV in basis II), 13.1 eV for $\pi$ MO's (13.4 eV), and 18.2 eV for $\delta$ MO's (17.3 eV). Thus, both bases predict noticeable contributions of these types of MO to the bonding. Whereas the $\delta$ MO's turn out to be the more deeply stabilized, the $\sigma$ MO's show the larger $g$–$u$ splitting at all values of $R$. The new result from basis II is the lowering of the $\sigma(4s)$ MO's (not shown in Table III). This effect would make possible the $s$–$d$ hybridization. Such mixture is totally out of question in basis I, given the too high energy of the empty 4$s$ orbital, as discussed under Method.

TABLE III

MOLECULAR ORBITAL (MO) ENERGIES (a.u.) OF THE 3$d$ STATES OBTAINED FROM THE SCF SOLUTION OF THE $^5\Sigma_g^+$ STATE

| | $R(Ni^{2+}–Ni^{2+})$, a.u. | | | | | |
|---|---|---|---|---|---|---|
| MO | 3.20 | 3.45 | 3.60 | 4.20 | 4.45 | ∞ |
| $\sigma_g$ | −1.298 | −1.224 | −1.187 | −1.080 | −1.048 | −0.7011 |
| | −2.030 | −1.973 | −1.941 | −1.835 | | −1.4076 |
| $\sigma_u$ | −1.137 | −1.126 | −1.116 | −1.063 | −1.039 | |
| | −1.838 | −1.822 | −1.811 | −1.766 | | |
| $\pi_g$ | −1.217 | −1.189 | −1.171 | −1.100 | −1.073 | |
| | −1.894 | −1.874 | −1.861 | −1.806 | | |
| $\pi_u$ | −1.284 | −1.225 | −1.195 | −1.104 | −1.075 | |
| | −2.029 | −1.969 | −1.938 | −1.840 | | |
| $\delta_g$ | −1.438 | −1.395 | −1.372 | −1.294 | −1.267 | |
| | −2.111 | −2.070 | −2.048 | −1.973 | | |
| $\delta_u$ | −1.430 | −1.392 | −1.370 | −1.294 | −1.267 | |
| | −2.087 | −2.054 | −2.036 | −1.969 | | |

*Note*. First row entries correspond to basis I; second row entries to basis II.

The results of our limited CI can be seen in Table IV. Large stabilizations are produced by this limited CI, particularly for the $^3\Sigma_g^-$ state. Accordingly, this state becomes the lower multiplet among those considered in the diagonal calculation. A larger CI could lower the $^5\Sigma_g^+$ state (unaffected by the CI considered here) and, in general, modify the present prediction. One can argue, however, that in $Ni_2^{4+}$ the partners of this quintet are probably too high to transform it into the ground state of the dimer.

It is clear that the nonempirical determination of the ground state requires a great number of large scale CI calculations. In the absence of such high-quality calcula-

TABLE IV

CI ENERGIES OF THE $^3\Sigma_g^-$ AND $^1\Sigma_g^+$ STATES OF THE Ni$_2^{4+}$ ION

| | $R$(Ni$^{2+}$–Ni$^{2+}$), a.u. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| State | 3.20 | 3.45 | 3.60 | 4.20 | 4.45 | 4.70 | 4.95 | 5.20 |
| $a\ ^3\Sigma_g^-$ | 8.0776 | 7.9619 | 7.9127 | 7.8215 | 7.8200 | 7.8332 | 7.8569 | 7.8872 |
| | 5.6513 | 5.4972 | 5.4345 | 5.3266 | | | | |
| $b\ ^3\Sigma_g^-$ | 1.1944 | 1.2366 | 1.2726 | 1.4656 | 1.5612 | 1.6618 | 1.7644 | 1.8664 |
| | −0.7739 | −0.7765 | −0.7573 | −0.5906 | | | | |
| $a\ ^1\Sigma_g^+$ | 7.4171 | 7.4507 | 7.4822 | 7.6602 | 7.7508 | 7.8469 | 7.9455 | 8.0439 |
| | 4.8955 | 4.8846 | 4.8994 | 5.0515 | | | | |
| $b\ ^1\Sigma_g^+$ | 5.3261 | 5.3068 | 5.3097 | 5.3922 | 5.4500 | 5.5167 | 5.5887 | 5.6628 |
| | 3.0491 | 2.9872 | 2.9745 | 3.0343 | | | | |
| $c\ ^1\Sigma_g^+$ | 5.0195 | 4.9928 | 4.9917 | 5.0608 | 5.1140 | 5.1765 | 5.2448 | 5.3155 |
| | 2.7793 | 2.7103 | 2.6937 | 2.7405 | | | | |
| $d\ ^1\Sigma_g^+$ | 3.9036 | 3.8499 | 3.8342 | 3.8547 | 3.8913 | 3.9388 | 3.9935 | 4.0519 |
| | 1.7991 | 1.7047 | 1.6743 | 1.6744 | | | | |
| $e\ ^1\Sigma_g^+$ | 3.5394 | 3.4718 | 3.4486 | 3.4440 | 3.4720 | 3.5118 | 3.5595 | 3.6115 |
| | 1.4553 | 1.3473 | 1.3096 | 1.2854 | | | | |

*Note*. First row entries correspond to basis I; second row entries to basis II. All numbers referred to −3006.0 a.u.

tions, some information can be gained by comparing the results predicted by a simpler calculation with the available theoretical and experimental data. In this context, the equilibrium properties of the $^3\Sigma_g^-$ and the $^1\Sigma_g^+$ states collected in Tables II and V can be compared to the results obtained in analogous systems. First, we observe that $R_e(^3\Sigma_g^-)$ is reduced by CI from 2.03 to 1.76 Å. Comparable reductions have been observed in Ni$_2$ by Shim *et al.* (*9*): $R_e$ = 2.60 Å (SCF) to 2.20 Å (CI), and by Noell *et al.* (*17*): $R_e$ = 2.43 Å (generalized valence-bond (GVB) method) to 2.26 Å (single and double excitation CI method, SDCI). A second comparison can be made with the results on Ni$_2$ and Ni$_2^+$ obtained by Upton and Goddard (*8*). They found, by using the polarization of occupied orbitals-configuration interaction (POL-CI) method, $R_e$ = 2.04 Å for Ni$_2$ and $R_e$ = 1.96 Å for the ion. This result makes our $R_e$ = 1.76 Å, obtained with basis II after CI, a reasonable estimate for the Ni$_2^{4+}$ system.

TABLE V

EQUILIBRIUM PROPERTIES OF THE $^3\Sigma_g^-$, $^1\Sigma_g^+$ STATES OF Ni$_2^{4+}$ AFTER CI

| State | $E_e$ (a.u.) | $R_e$ (a.u.) | $D_e$ (eV) | $\omega_e$ (cm$^{-1}$) |
|---|---|---|---|---|
| $^3\Sigma_g^-$ | −3004.8236 | 2.92 | 40.34 | 665 |
| | −3006.7808 | 3.33 | 34.70 | 814 |
| $^1\Sigma_g^+$ | −3002.5692 | 3.91 | | 551 |
| | −3004.7248 | 3.97 | | 617 |

*Note*. First row entries correspond to basis I; second row entries to basis II.

Unfortunately, there are no experimental data available for direct comparison with our results in Tables II and V. However, some idea about their plausibility can be gained by analyzing them in terms of some well-known correlations among different molecular constants in diatomics. We briefly comment on two of such relationships. First, there is the linear dependence between the quantity $(\omega_e^2\mu)^{-1/3}$ and $R_e$ predicted by Badger (*18*) and examined by Wolf and Schmidtke (*15*) over the series of (neutral) first-row transition diatomics. Our results follow quite closely such a linear correlation displayed in Fig. 6 of Ref. (*15*). Second, according to Mecke (*19*), the product $R_e^3 \cdot \omega_e$ should be a constant (about 3000 if $\omega_e$ is in $cm^{-1}$ and $R_e$ in Å). The nonempirical spectroscopic constants can deviate from such a value by 30% or more (up to 100% for $Sc_2$, (*15*)). Our results deviate by some 50% from this constant.

We conclude by discussing our approximate results in connection with the question of the $Ni^{2+}$–$Ni^{2+}$ interaction in the $Ni^{2+}$ thiocarboxylates. In these dimers, $R_e(Ni^{2+}$–$Ni^{2+})$ = 4.70 a.u. (*3, 4*). If we accept that our prediction of $R_e$ for the $Ni_2^{4+}$ ion *in vacuo* is plausible, the large difference between 3.33 a.u. (basis II, CI) and 4.70 a.u. suggests that in the thiocarboxylates there are other forces, different from the metal–metal interaction, determining the equilibrium positions of the $Ni^{2+}$ ions. If we recall the estimation made above about the gradient of the short-range, noncoulombic interaction, we can suggest that the equilibrium geometry of the $Ni^{2+}$ thiocarboxylates is probably determined by the interactions of the nickel ions with the surrounding oxygen and sulfur atoms. In our previous analysis of these thiocarboxylates in terms of crystal-field calculations (*6*), we were able to give a reasonable interpretation of the optical spectrum of these systems by taking into account the point-charge perturbation of the oxygen and sulfur atoms on the 3*d* AO's of the two $Ni^{2+}$ ions. In such calculation, the classical crystal-field parameters needed for clusters like $NiO_4$, $NiO_5$, $NiS_4$, etc., were taken from analogous systems, after a detailed study of their intersystem transferability. According to these calculations, the $Ni^{2+}$ ion surrounded by four sulfur atoms ($Ni^A$) would have a $^1A_{1g}$ ground state, and the other $Ni^{2+}$ ion ($Ni^B$), surrounded by four oxygens in the dealcoholated species and by fives oxygens in the alcoholated one, would be in a $^3B_1$ state, i.e., both nickel ions would have orbitally nondegenerate ground states and the spin distribution would be $S^A = 0$, $S^B = 1$ (*6*). The inclusion of the metal–metal interaction, through the point-charge perturbation of the $Ni^A$ on the $Ni^B$ $O_4$ cluster and the perturbation of the $Ni^B$ on the $Ni^A$ $O_4$ cluster, did not change the spin distribution, nor the nondegenerate character of these ground states, but reduced the quantitative agreement between the crystal-field calculations and the observed optical spectrum of the thiocarboxylates.

Finally, we would like to comment on the relation between our predicted ground state for the $Ni_2^{4+}$ ion, $^3\Sigma_g^-$, and the discussion of the magnetic susceptibility and optical spectra of the $Ni^{2+}$ thiocarboxylates. We can suppose that, if the $Ni^{2+}$–$Ni^{2+}$ interactions were the main factors in setting the electronic structure of the $\{Ni(CH_3$–$COS)_2\}_2$ compounds, the effect of the oxygen and sulfur atoms could be approximated by electrostatic perturbations, as in crystal-field theory. Such perturbations would not change the spin state of the $Ni_2^{4+}$ ground state (in the absence of the spin–orbit interaction), nor its nondegenerate spatial wavefunction, if we assume that it is a $\Sigma$ state, as predicted by our CI calculation. Within such electrostatic approach, the magnetic properties of the $\{Ni(CH_3$–$COS)_2\}_2$ compounds could be discussed, in first order, in terms of the magnetism deducible from the ground state of the $Ni_2^{4+}$ ion. We recall that a $^3\Sigma_g^-$ ground state, with total spin $S = 1$, would be compatible with the reported magnetic moment of several thiocarboxylates, corresponding to the presence of two unpaired electrons per dimer (*3*). The interpretation of the observed spectra (*3*) would require, however, the presence of several multiplets, with the same spin as the ground state, in the visible window. This is not the case in our calculation. It is true that we have not considered here configurations with $\sigma$ or $\pi$ open-shells. Results on $Ni_2$ and $Ni_2^+$ (*8*) suggest that transitions involving such open-shells should be above the $\delta$–$\delta$ transitions discussed in this work. A quantitative examination of those electronic transitions is beyond the aim of this paper. From the behavior of the orbital energies computed here (basis II, Table III) we see that at $R = 3.60$ a.u. $\Delta\varepsilon(\delta\delta) = \varepsilon(\delta_u) - \varepsilon(\delta_g) = 0.3$ eV, the next smaller $\Delta\varepsilon$ being $\Delta\varepsilon(\sigma\delta) = \varepsilon(\sigma_g) - \varepsilon(\delta_g) = 2.9$ eV. If this $\Delta\varepsilon(\delta\delta)$ gives rise to $\delta_g \rightarrow \delta_u$ electronic transitions, such as those discussed in this paper, with transition energies measured as differences in total energy, $\Delta E$, in the visible region of the spectrum, we could think that electronic transitions involving $\delta_g \rightarrow \sigma_g$ excitations would have transition energies, $\Delta E$, well above the visible window.

From this discussion we can conclude that, with the reserves due to the use of very small basis set and the absence of an extended CI, our calculation on the $Ni_2^{4+}$ ion suggests that the metal–metal interactions are not determinant factors in the electronic structure and geometry of the $\{Ni(R\text{–}COS)_2\}_2$ dimers. This suggestion agrees with the arguments deduced from our previous crystal-field analysis on these thiocarboxylates (*6*), and supports the point of view held by Melson *et al.* (*3, 4*), on this problem.

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