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Crystal-Field Calculation of the 3*d* Multiplets of the Binuclear Ni(II) Monothiocarboxylates

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The electronic spectra of the dimers $(Ni(R\text{-}COS)_2)_2$ and $(Ni(R\text{-}COS)_2)_2 \cdot C_2H_5OH$ are calculated by crystal-field theory in terms of different polyhedra of coordination around the two Ni^{2+} ions. The necessary radial parameters are taken from other clusters of Ni^{2+} after a detailed study of their intercluster transferability. The calculations are organized in two blocks. In the first one, the Ni^{2+}–Ni^{2+} interaction is neglected and the clusters Ni^AS_4, Ni^BO_4, and Ni^BO_5 are considered. In the second block, this interaction is explicitly taken into account as a point-charge perturbation produced by one of the two metal ions on the 3*d* states of the other one. Accordingly, we deal with the $Ni^AS_4Ni^B$, in which the Ni^B acts as a pointlike ligand of charge q, and with the $Ni^BO_4Ni^A$ and the $Ni^BO_5Ni^A$, where the Ni^A is the punctual ligand. The calculation shows that the optical spectra and magnetic moments of these dimers can be best reproduced if $q \simeq 0$, i.e., when the metal–metal electrostatic interaction is negligible. The agreement with the experiments quickly disappears as q grows. This calculation supports the interpretation of Melson *et al.* (*Inorg. Chem.* **9**, 1116 (1970)) according to which the 3*d* electronic distribution of the Ni^{2+} ions in these dimers is probably controlled by their nearest neighbors rather than by the metal–metal interaction.

I. Introduction

The Ni^{2+} ion reacts with monothiocarboxylic acids to form binuclear compounds that show bridging acetate cage structures (*1–3*). In these structures the two nickel ions have different environments: one is surrounded by four sulfur atoms and the other one by four oxygen atoms. We shall call them from now on Ni^A and Ni^B, respectively. The internuclear separation between the two nickel ions turns out to be 2.49–2.50 Å (*2, 3*), about the same as in metallic nickel (*4*). The room temperature optical spectra and magnetic susceptibility of the thioacetate, thiopropionate, and thiobenzoate, all having an ethanol molecule per dimer, have been reported by Melson *et al.* (*1*). The three compounds have magnetic moments in the range 2.2 to 2.4 μ_B and obey the Curie–Weiss law between 80 and 300 K, with small values of the Weiss constant (*1*). All these experimental facts have been interpreted by Melson *et al.* (*1*) assuming that the valence electronic distributions around the two nickel ions are determined by the interactions of the metallic ions with their closest neighbors. If this were so, the significance of the metal–metal interaction in the stabilization of this molecular structure could be ruled out. However, Bonamico *et al.* (*3*) interpreted the short nickel–nickel distance and the observed twisting of the two intersecting rings bridg-

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ing the nickel ions in these clusters as indications of a metal–metal bond. Furthermore, Oro *et al.* (*5*) prepared the dealcoholated Ni(II) monothioacetate and Ni(II) monothiobenzoate and found that these compounds have magnetic moments and powder diffraction diagrams very similar to those corresponding to the alcoholated compounds. Based on that evidence, Oro *et al.* (*5*) suggested that a metal–metal bond probably exists in this type of compounds, too.

These two opposite interpretations clearly represent two different views of the open-shell electronic distributions in these clusters. Such different distributions should give rise to experimentally observable differences, one of the most significant being the distribution of the total electronic spin S between the two nickel atoms. According to the first interpretation (*1*), the strong field of the sulfur ligands on the Ni^A would ensure a singlet ground state in this ion, i.e., S^A (the total electronic spin of the Ni^A) would be zero. On the other hand, the Ni^B, surrounded by oxygen ligands, would have a triplet ground state ($S^B = 1$). In this way the spin of the dimer would be in agreement with the observed magnetic moments. By invoking a mainly covalent bond between the two nickel ions, the alternative approach assumes the pairing of two $3d$ electrons, one from each ion, in a molecular orbital. The two remaining unpaired $3d$ electrons would give rise to a spin distribution close to $S^A = \frac{1}{2}$, $S^B = \frac{1}{2}$.

Questions such as the electron spin distribution between these two metal ions can be investigated by ESR spectroscopy, but these measurements have not yet been published. On the other hand, the general characteristics of the electronic distributions in the cluster could be deduced from a detailed theoretical investigation. However, in compounds as big as those discussed here a much simpler analysis, based upon the crystal-field predictions, could be rather helpful in the description of the multiplets of the nickel ions and, therefore, in the understanding of the optical spectrum and the temperature dependence of the magnetic susceptibility of the dimer. To be reliable, this analysis should be of an empirical nature and its predictions based on the use of the best crystal-field parameters, selected from previous experience.

In this work we present the results of several crystal-field calculations of the $3d$ multiplets of the two nickel ions in these cage structures. This study was undertaken as the first step of a more complete theoretical investigation which will include a SCF MO calculation of the electronic structure of the dimer. Our calculations are based on the consideration of different polyhedra of coordination around the Ni^A and Ni^B. Such polyhedra are defined according to the interactions considered to be significant. The possible nickel–nickel interaction is simulated in these calculations, as with any bond in crystal-field theory, by a point-charge perturbation of a (positive) ligand, say the Ni^B, on the other metal ion. The best radial parameters necessary to compute the eigenvalues of the appropriate perturbing matrices are selected from spectral data of well-known complexes after a detailed study of their transferability (*6*). As a result of this study, the parameters used in this work are those felt to be most appropriate out of a collection generated by means of an objective and systematic fitting of the electrostatic matrices to many experimentally observed Ni(II) spectra.

The main conclusion from the present work is that the observed magnetic moments and optical spectra of these dimers (*1*) can be explained in the framework of the crystal-field theory without invoking an effective nickel–nickel interaction. Therefore, our analysis supports the point of view of Melson *et al.* (1). Whereas this result was predicted upon qualitative crystal-field grounds in the alcoholated compounds, in view of the pentacoordination around the Ni^B, our calculation shows that the same picture arises in the dealcoholated species, where the Ni^B presents a square-planar tetracoordination of oxygen ligands. Within this limited and approximated description, the most probable spin distribution on the two nickel ions seems to be, then, $S^A = 0$, $S^B = 1$.

In the next section we present the details of our calculation and in Section III the results and discussion.

II. Method

We divide our work into two sets of calculations. In calculation I, we neglect any metal–metal interaction and see the dimer as formed by two independent tetracoordinated nickel ions: the square-planar Ni^AS_4 and Ni^BO_4. That corresponds to the situation in the dealcoholated compounds. In the dimer originally reported by Melson *et al.* (*1*), the second cluster becomes a square-pyramidal polyhedron Ni^BO_5. In calculation II, the nickel–nickel interaction is switched on and we then have a pentacoordinated Ni^A surrounded by four sulfur atoms in the equatorial plane, and the Ni^B, as fifth ligand, on the vertical axis. In the dealcoholated compounds the Ni^B is also pentacoordinated: four oxygen in the xy plane and the Ni^A on the z axis. In the alcoholated compounds the Ni^B has a pseudooctahedral coordination $Ni^BO_5Ni^A$. It should be noted that in calculation II we deal with negative and positive ligands within a single cluster.

In our calculation we use the geometry of the dimer determined by Melson *et al.* (*2*) and the weak field electrostatic matrices without the spin–orbit interaction (*7, 8*). To deal with the radial parameters we adopt the criteria that gave good results earlier (*6, 9*); each type of ligand is represented by a classical parameter $\Delta = 5qG^4(R_{ML})/3$, where q is the perturbing charge associated with the ligand, R_{ML} the internuclear metal–ligand distance and $G^4(R_{ML})$ the fourth-order splitting integral (*10*)

$$G^4(R_{ML}) = \left\langle R_{3d}(r) \left| \frac{r_<^4}{r_>^5} \right| R_{3d}(r) \right\rangle.$$

In this formula $r_<$ is the lesser and $r_>$ the greater of r and R_{ML}, and $R_{3d}(r)$ is the $3d$ metallic wavefunction. All the splitting integrals of order $\neq 4$ appearing in fields of symmetry lower than O_h can be written out as functions of the Δ and the scaling factor λ of $R_{3d}(r)$. This function becomes $R_{3d}(r \cdot \lambda_{opt})$ after the fitting process. As in our earlier work, we use the approximate Hartree–Fock 2-ζ $R_{3d}(r)$ of Richardson et al. (*11*) as reference ($\lambda = 1$) wavefunction. All the interelectronic repulsion integrals appearing in the crystal-field matrices are completely determined by the reference $3d$ wavefunction and λ (*9*)

$$F^k(3d, 3d; \lambda) = \lambda \cdot F^k(3d, 3d, \lambda = 1).$$

In conclusion, our radial parameters are λ and a Δ for each type of ligand species in the cluster.

In the selection of parameters from data obtained from other Ni^{2+} clusters we follow the rules discussed earlier (*6*), namely (a) the parameters Δ are transferable within a margin of 10% among clusters formed by chemically analogous ligands, (b) differences in internuclear distances from cluster to cluster are taken into account by means of the R_{ML}^{-5} law $\Delta(R_{ML})/\Delta(R'_{ML}) = (R'_{ML}/R_{ML})^5$, and (c) the scaling factor λ is transferable through some addition rules equivalent to the rule of average environment (*12*). These three rules are sufficient to deal with all clusters appearing in calculation I. In calculation II we also need parameters for the nickel ion as a ligand. As such information is not available, we prepare a variety of transition energy diagrams whose x axes are labeled by the effective charge of the perturbing nickel. According to the rule (c) stated above, λ has an uncertainty of about

20% (one bond in five) in the pentacoordinated clusters which contain a positive nickel as fifth ligand. Consequently, we examine several diagrams, prepared with different values of λ, to cover this range of of uncertainty.

III. Results and Discussion

A. Calculation I

We compute the energy levels of the tetracoordinated $\mathrm{Ni}^A\mathrm{S}_4$ with parameters which originate from the analysis of the octahedral NiS_6 cluster. From the spectrum of the hexakis(*N*,*N*′-di-*n*-butylthiourea) nickel(II) iodide, reported by Tarantelli *et al.* (*13*), we obtain the optimum set $\Delta(\mathrm{S}) = 8.7$ kK and $\lambda = 0.40$. Since there is a single type of metal–ligand bond in NiS_6 and NiS_4, we shall assume that this value of λ is transferable from the octahedral to the square-planar cluster. This assumption seems reasonable in view of the behavior of λ in the systems NiO_6, NiN_6, and $\mathrm{NiN}_4\mathrm{O}_2$, discussed in Ref. (*6*), and we shall adopt it again in the calculation of the energy levels of the $\mathrm{Ni}^B\mathrm{O}_4$. The selection of a value for $\Delta(\mathrm{S})$ in $\mathrm{Ni}^A\mathrm{S}_4$ deserves some comment.

First, the R_{ML}^{-5} law transforms $\Delta(\mathrm{S})$ from 8.7 to 15.4 kK, since $R_{\mathrm{ML}}(\mathrm{Ni–S}) = 2.50$ Å in the octahedral cluster (*14*) and 2.23 Å in the dimer (*2*). Moreover, we have to consider that whereas the butylthiourea is a neutral ligand, the sulfur atoms in the dimer belong to a thiocarboxylate anion. An analogous change in the case of oxygen-containing ligands (for instance, a change from oxygen of a water molecule to oxygen of a carboxylate anion) gives rise to increments in $\Delta(\mathrm{O})$ of about 2 kK (*6*). In this case we should expect a greater effect since the Ni(II) complexes with sulfur-containing ligands are known to show large variations in the value of Δ. Jørgensen quoted variations larger than 50% (*15*). These variations have been related to the relatively larger number of electrons in sulfur, to the operation of π-bonding effects and, in general, to an inadequacy of the crystal-field approach. In an analogous way, one can attribute such variations to changes in the chemical environment of the ligand species. To have an estimation of the variations in $\Delta(\mathrm{S})$ appropriate to our case we prepare Fig. 1 in which the lower excited states of the $\mathrm{Ni}^A\mathrm{S}_4$ are plotted against $\Delta(\mathrm{S})$. Following our hypotheses, these multiplets are calculated with $R_{\mathrm{ML}}(\mathrm{Ni–S}) = 2.23$ Å and $\lambda = 0.40$. We recall that this diagram was discussed by Maki (*7*) in a slightly different manner. Our results, shown in Fig. 1, are in complete agreement with her calculations.

In Fig. 1 we also plot five experimental observations. The absorption at 20.0 kK is given by Melson *et al.* (*1*) and assigned by them to the $\mathrm{Ni}^A\mathrm{S}_4$ cluster. The other four have been observed by Jørgensen in the diethyldithiophosphate (dtp) and the diethyldithiocarbamate (dtc) of Ni(II) (*15*). According to the calculation presented in Fig. 1, we obtain the best agreement with these experiments if the bands near 15 kK are assigned to the transition $a^1A_{1g} \rightarrow a^1B_{2g}$ and the bands near 20 kK to the $a^1A_{1g} \rightarrow a^1E_g$. Melson *et al.* (*1*) suggested that the absorption at 20 kK could be assigned to the $a^1A_{1g} \rightarrow A_{2g}$. From our calculation we can suggest that if this peak comes from the Ni^A center, its assignment to the $a^1A_{1g} \rightarrow a^1E_g$ transition seems more probable. Furthermore, a second peak at about 16 kK ($a^1A_{1g} \rightarrow a^1B_{2g}$) should be observable. It is interesting to note that Melson *et al.* (*1*) observed a peak at 15.5 kK which they assigned to the Ni^B center. Our calculation shows that this peak could be assigned, alternatively, to the Ni^A center.

Let us now consider the $\mathrm{Ni}^B\mathrm{O}_4$ cluster appearing in the dealcoholated compounds (*5*). As commented above, we shall use in this cluster the value of λ obtained in the analysis of many NiO_6 clusters (*6*), i.e., $\lambda = 0.71$. On the other hand, we shall compute

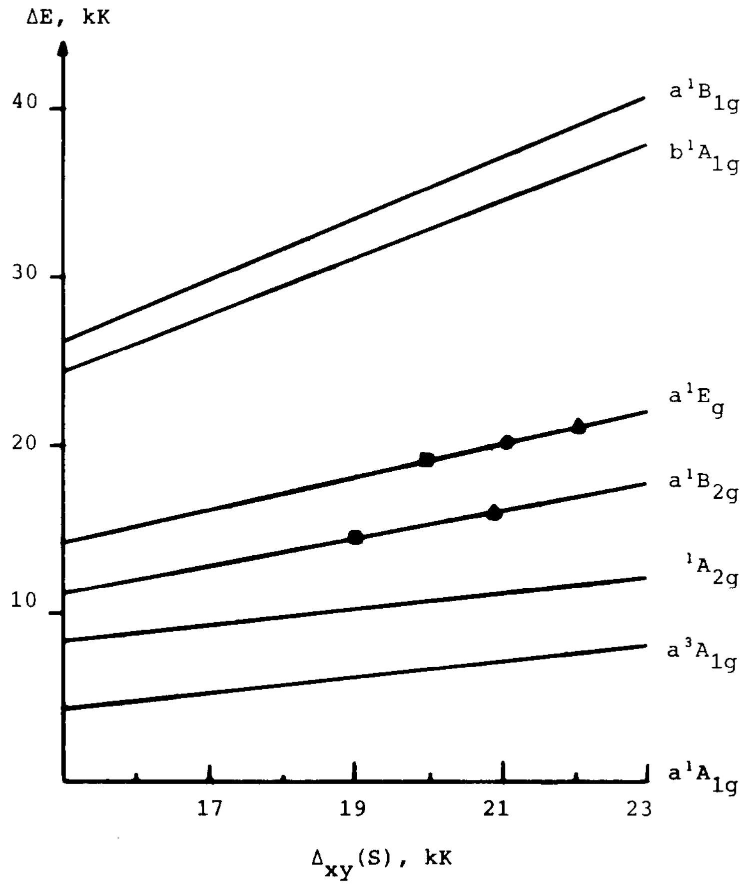

FIG. 1. Transition energies (kK) of the Ni^{A}S$_4$ in (Ni(RCOS)$_2$)$_2$ computed from the ground state a^1A_{1g} as functions of the sulfur field strength Δ_{xy}(S). R_{ML}(Ni–S) = 2.23 Å and $\lambda = 0.40$. ■ Ni(dtp)$_2$, Ref. (15); ▲ Ni(dtc)$_2$, Ref. (15); ● (Ni(RCOS)$_2$)$_2$ · C$_2$H$_5$OH, Ref. (1).

the energy levels of this species with several values of Δ(O), all of them estimated from the analysis of the axial perturbations produced by the carboxylate anions in the Ni(stien)$_2^{2+}$ complexes (stien = 1,2 diphenylethylenediamine). The spectra of these complexes have been measured by Zink and Drago (16). Although the crystal structure of the Ni(stien)$_2$(Cl$_2$CH–COO)$_2$ has been reported (17) and the Ni–O distances are 2.14 ± 0.02 Å, we analyze all the spectra of the Ni(stien)$_2^{2+}$ complexes with a common value of R_{ML}(Ni–O) = 2.10 Å, an average value obtained from many crystallographic determinations. We obtain Δ(O) = 9.5 kK. The Ni–O distances in the dimer are 2.04 ± 0.03 Å (2). The R^5_{ML} law, therefore, changes Δ(O) to 11.0 kK. We assume, further, that the changes in chemical environment from chloroacetates to the thioacetate produce very minor corrections in Δ(O). Accordingly, we compute the energy levels of the Ni^{B}O$_4$ with Δ(O) = 11.0 ± 1.0 kK and $\lambda = 0.71$ and find that in this range of parameters the ground state of the cluster is always the $^3B_{1g}$. Donini *et al.* (18) have shown that the high-spin square-planar nickel compexes may exist with a ^3E_g ground state if the equatorial ligands are strong π donors; otherwise the ground state is the $^3B_{1g}$. Our results are in agreement with their calculations. The magnetic moment of a $^3B_{1g}$ ground state is essentially independent of the temperature but the magnetic moment of a ^3E_g ground state is temperature dependent and highly anisotropic (*18*). Therefore, the results of our calculation agree with the temperature-independent paramagnetism reported in the dealcoholated compounds (*5*). The presence of the $^3B_{1g}$ as the ground state of the Ni^BO_4 is very interesting because it shows that the interpretation of Melson *et al.* (*1*) would be not affected by the dealcoholation of the dimer. If one assumes (*5*), on the contrary, that such dealcoholation produces a Ni^BO_4 with a singlet ground state the dealcoholated dimer should be diamagnetic, contradicting the experimental evidence. From this assumption Oro *et al.* (*5*) concluded that the electronic distribution in the dimer had to be governed by the Ni–Ni interaction rather than by the nearest-neighbor interactions. The results of the present calculation do not support this conclusion.

According to our calculations the dealcoholated dimers should show four electronic transitions, near 6–7 kK ($^3B_{1g} \rightarrow a^3E_g$), 10–12 kK ($\rightarrow {}^3B_{2g}$), 12–14 kK ($\rightarrow b^3E_g$), and 23–26 kK ($\rightarrow b^3A_{2g}$), in addition to the two bands associated with the Ni^AS_4 already discussed. The optical spectra of these dealcoholated species have not been reported (*5*).

The alcoholated compounds contain the pentacoordinated Ni^B in Ni^BO_5. We compute the multiplets of this cluster with $\Delta_{xy}(O) = 11 \pm 1$ kK and $\Delta_z(O) = 8$ kK. This value of $\Delta_z(O)$ is the average result of several calculations on Ni(II) complexes with neutral ligands, such as water, mathanol, ethanol, etc., reported in Ref. (*6*). We now use R_{ML}(Ni–O) = 2.05 Å, as in Ref. (*6*), for the bond along the *z* axis of the cluster, making the R_{ML}^{-5} correction unnecessary. Finally, we use $\lambda = 0.71$ as in the Ni^BO_4. The ground state turns out to be the $^3B_1$ in the three calculations. The change in $\Delta_{xy}(O)$ produces moderate effects in the lower triplets. Our best calculation turns out to be that with $\Delta_{xy}(O) = 12$ kK and it gives rise to the transition energies $^3B_1 \rightarrow a^3E = 6.2$ kK, $\rightarrow a^3A_2 = 8.2$ kK, $\rightarrow {}^3B_2 = 12$ kK, $\rightarrow b^3E = 17$ kK, and $\rightarrow b^3A_2$ 27 kK. These numbers agree rather well with the spectrum reported by Melson *et al.* (*1*), namely, 7.7, 12.5, 15.5, and 27 kK, although we find deviations smaller than 0.6 kK in the peaks at 7.7 (a^3A_2), 12.5 ($^3B_2$), and 27 kK (b^3A_2) and a deviation of 1.5 kK in the peak at 15.5 kK. With $\Delta_{xy}(O) = 10$ and 11 kK, the general agreement is also reasonable but this difference in deviations persists. Such difference suggests, again, that the peak at 15.5 kK could be associated with the Ni^A center. Apart from this alternative interpretation of the peak at 15.5 kK, our results support the spectral interpretation given in Ref. (*1*) and indicate that the criteria we adopt in the manipulation of the crystal-field parameters seem appropriate. The comparison of these results with those obtained in the Ni^BO_4 leads to the conclusion that the dealcoholation should have rather minor effects on the optical spectra of these dimers.

B. Calculation II

We now take into account the Ni–Ni interaction. First, we examine the energy levels of the pentacoordinated Ni^A in the $Ni^AS_4Ni^B$. In accordance with our hypotheses, we estimate the parameter λ by means of the addition rule (*6*) $\lambda(\text{cluster}) = (4\lambda_{xy}(\text{Ni–S}) + \lambda_z(\text{Ni–Ni}))/5$. As discussed above, we shall use for λ_{xy}(Ni–S) the value obtained from the octahedral cluster NiS_6, i.e., $\lambda_{xy} = 0.4$. We still need the unknown λ_z(Ni–Ni). Allowing for a total uncertainty in λ_z (from $\lambda_z = 1$ to $\lambda_z = 0$), we consider three possible cases: $\lambda_z = 0$, 0.5, and 1, giving λ(cluster) = (0.3, 0.4, and 0.5, respectively.

In dealing with $\Delta_{xy}(S)$ we recall from calculation I that the value obtained from NiS_6 is transformed into 15.4 kK by the R_{ML}^{-5} correction. We do not know the further correction we should make on this figure to incorporate the effects of the chemical environment of the sulfur atoms. We have already quoted that such effects are of about 2 kK in oxygen complexes of Ni^{2+} and are expected to be larger in sulfur complexes. Thus, we should use a value of $\Delta_{xy}(S)$ larger than 18 kK. In Fig. 1 we see that the observations made by Jørgensen (*15*) are compatible with any $19 \leq \Delta_{xy}(S) \leq 22$ kK. We have adopted this range and performed calculations with $\Delta_{xy}(S) = 19, 20$, and 21 kK. That makes nine possible pairs $\Delta_{xy}(S)$, λ(cluster). To deal with the unknown axial field strength, $\Delta_z(Ni^B)$, we prepare nine transition energy diagrams, corresponding to these nine pairs, with $\Delta_z(Ni^B)$ as independent variable. Since $\Delta_z = 5q_zG^4(R_z,\lambda)/3$, we compute G^4 with R_z(Ni–Ni) = 2.5 Å, the observed value (*2*), and use q_z as independent variable.

As an example of this calculation, we present the diagram corresponding to $\Delta_{xy}(S) = 21$ kK and $\lambda(\text{cluster}) = 0.40$ in Fig. 2. We choose this particular diagram because it contains at $q_z = 0$ the same information as on the vertical line at $\Delta_{xy}(S) = 21$ kK in Fig. 1. That makes the comparison between calculations I and II straightforward. It should be noted, however, that the main features we are going to comment on in this figure are present in the other eight diagrams. For instance, the ground state is the a^1A_1 in all of them. The energy of most multiplets is a linear function of q_z, with a slope that increases (in absolute value) when λ(cluster) decreases. In Fig. 2 we plot the lower singlets and the lowest triplet, the a^3A_2. This triplet tends to become the ground state when q_z increases, but its crossing with the a^1A_1 appears at values of q_z to be unacceptably high. Therefore, the perturbation of the Ni^AS_4 by the axial positive charge representing the Ni^B does not produce a paramagnetic Ni^A if reasonable values of the crystal-field parameters are used.

In the quantitative interpretation of the optical spectrum we have to analyze two different assignments.

(a) There is only one band in the spectrum corresponding to the Ni^A center (the peak at 20 kK). This is the hypothesis of Melson *et al.* (*1*). Once we have chosen the values of $\Delta_{xy}(S)$ and λ(cluster) we can find the value of q_z that predicts a peak at 20 kK. Since we have explored nine pairs of $\Delta_{xy}(S)$ and λ(cluster), we have nine values of q_z. All of them range from 0 to 1 a.u. For instance, in the diagram represented in Fig. 2, $q_z = 0.5$ a.u. Obviously, we can find many different sets of parameters compatible with a peak at 20 kK, but we restrict this (in principle infinite) collection of parameters to these sets with $0.3 < \lambda(\text{cluster}) < 0.5$ and $19 < \Delta_{xy}(S) < 22$ in accordance with our hypotheses. The main problem with this assignment is that we always find a second peak at 20 ± 2 kK. For instance, in Fig. 2 we find the a^1B_2 at 20 kK ($q_z = 0.5$) and the a^1E at 21.6 kK. This second feature has not been observed.

(b) There are two bands associated with the Ni^A, at 15.5 and 20 kK, as suggested above. We still have many sets of parameters compatible with these two peaks but if we maintain our restrictions on $\Delta_{xy}(S)$ and λ(cluster) the values of q_z turn out to be very close to zero.

From these calculations we can conclude that, in the context of the crystal-field theory and within the approximations of our approach, the optical spectrum of the dimer can be better understood if $q_z \simeq 0$, i.e., when the electrostatic interaction is negligible.

Next, we compute the energy levels of the cluster $Ni^BO_4Ni^A$ in which the Ni^B shows pentacoordination. Again, we consider that $\Delta_{xy}(O) = 11.0 \pm 1.0$ kK, the values used in calculation I. As in $Ni^AS_4Ni^B$, we allow for variations in λ_z from 0 to 1 and

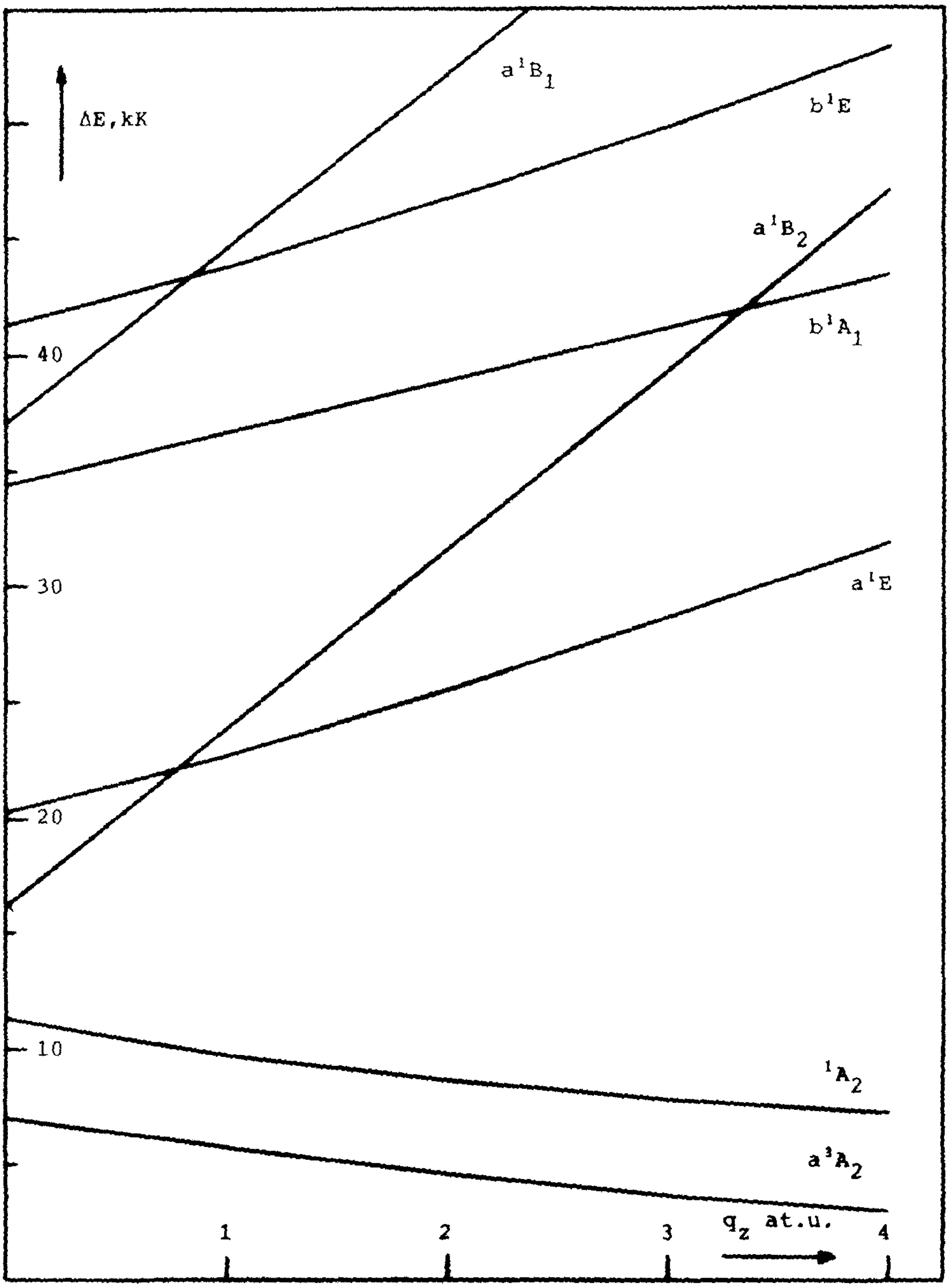

FIG. 2. Transition energies (kK) of the pentacoordinated $Ni^AS_4Ni^B$ computed from the ground state a^1A_1 as function of the Ni^B point charge q_z · R_{ML}(Ni–S) = 2.23 Å, R_{ML}(Ni–Ni) = 2.50 Å, Δ_{xy}(S) = 21 kK, and $\lambda = 0.40$.

perform calculations with $\lambda_{xy} = 0.71$, as in calculation I, having λ(cluster) = 0.6, 0.7, and 0.8. We again have nine pairs Δ_{xy}, λ(cluster) and nine corresponding energy level diagrams with $q_z(Ni^A)$ along the horizontal axis. From these diagrams we learn that the ground state of the $Ni^BO_4Ni^B$ is always a triplet. It turns out to be the $^3B_1$ if $q_z < 1$ a.u., and the a^3A_2 otherwise. Keeping λ(cluster) constant, the crossing point of these two triplets appears at smaller values of q_z when Δ_{xy} increases. For a given value of Δ_{xy} the crossing takes place at a value of q_z that decreases with λ(cluster). In any case, this pentacoordinated Ni^B would give rise to a temperature-independent paramagnetism. Since the spectrum of the dealcoholated dimer is unknown we will not discuss the details of this calculation and will pass to the final cluster we consider in this work.

We have to deal with the pseudooctahedral $Ni^BO_5Ni^A$, present in the alcoholated dimers and obtained from the Ni^BO_5 of calculation I by connecting the metal–metal interaction. As in calculation I, we use $\Delta_{xy}(O) = 11.0 \pm 1.0$ kK and $\Delta_z(O) = 8$ kK. The $\Delta_z(Ni^A)$ is the independent variable of the transition energy diagrams and λ(cluster) is computed as (5λ(Ni–O) + λ(Ni–Ni))/6. As before, we use λ(Ni–O) = 0.71 and

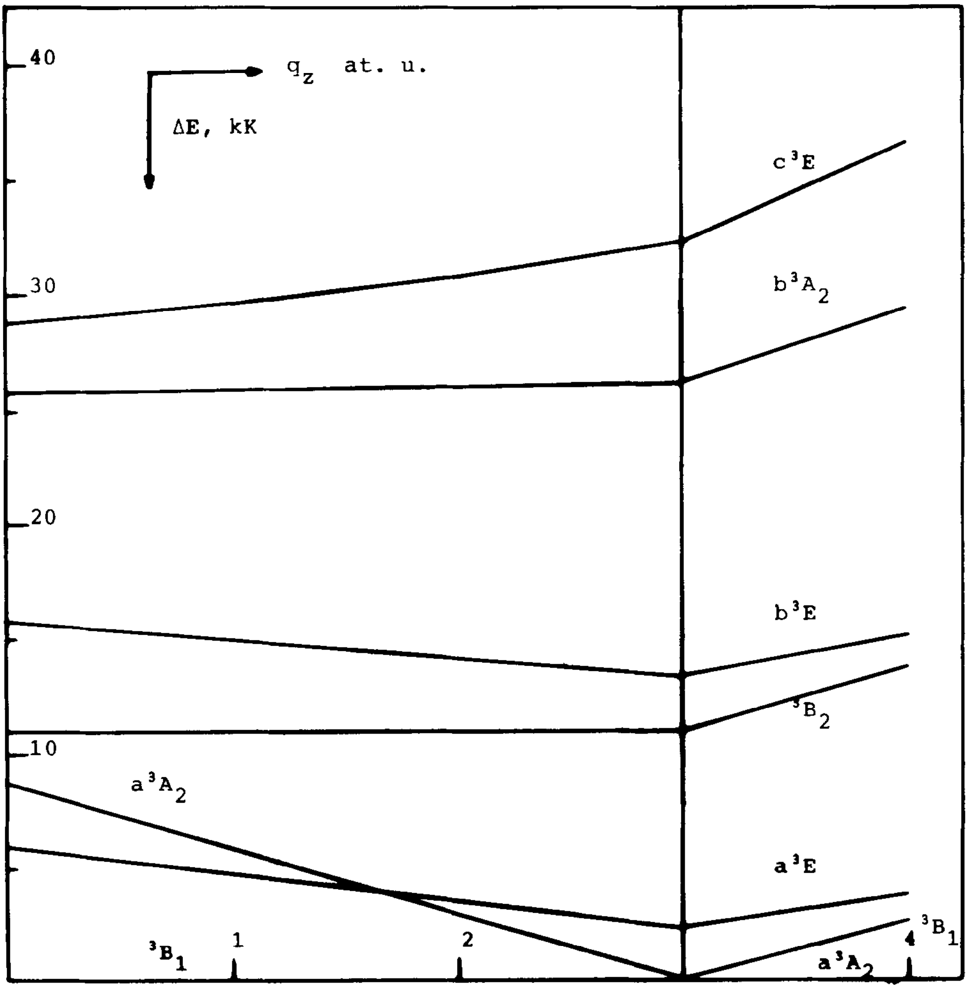

FIG. 3. Transition energies (kK) of the pseudooctahedral $Ni^BO_5Ni^A$ computed as functions of the Ni^A point charge $q_z \cdot R_{ML}(Ni\text{–}O) = 2.10$ Å, $R_{ML}(Ni\text{–}Ni) = 2.50$ Å, $\Delta_{xy}(O) = 11$ kK, $\Delta_z(O) = 8$ kK, and $\lambda = 0.70$.

three values for λ(Ni–Ni) 0, 0.5, and 1, giving λ(cluster) = 0.6, 0.7, and 0.8. We have again nine pairs $\Delta_{xy}(O)$, λ and nine corresponding diagrams. In Fig. 3 we show the results obtained with $\Delta_{xy}(O) = 11$ kK, $\Delta_z(O) = 8$ kK, and λ(cluster) = 0.7. As in $Ni^BO_4Ni^A$, there is a crossing of the $^3B_1$ with the a^3A_2 that converts the latter into the ground state for $q_z > 3$ a.u. The computed spectral frequencies are in good agreement with the data in Ref. (*1*), quoted above, only if q_z is very close to zero. In Fig. 3 we can observe that at $q_z = 0$ the transition energies are $^3B_1 \rightarrow a^3E = 6.0, \rightarrow a^3A_2 = 8.7, \rightarrow {}^3B_2 = 11, \rightarrow b^3E = 16, \rightarrow b^3A_2 = 26$, and $\rightarrow c^3E = 29$ kK. Again, comparable agreement appears with $\Delta_{xy}(O) = 12$ kK. In all these diagrams we see that the transition energies deviate progressively from the experimental data as q_z grows. The changes are small if $q_z < 1$ but quickly become significant for $q_z > 1$, and, in particular, when q_z has the nominal value ($q_z = 2$) the agreement is totally lost. We have, in essence, the same spectral behavior as in the case of the Ni^AS_4 perturbed by the punctual Ni^B; the consideration of the Ni–Ni interaction does not represent any improvement at all in the description of the optical spectra of the dimers.

The main conclusion of this work on binuclear Ni(II) monothiocarboxilates is that a crystal-field calculation carried out with reasonable values of the radial parameters can give an interpretation of the observed magnetic moments and optical spectra of these dimers without invoking a metal–metal interaction. When such interaction is taken into account as an electrostatic perturbation, the ground state of the Ni^A is not altered and that of the Ni^B can change from a $^3B_1$ to a $^3A_2$. Therefore, this electrostatic interaction does not change the spin distribution of the dimer. However, we find that the general good description of the optical spectra obtained in the calculation without metal–metal interaction disappears when the interaction is taken into account. This is so in the alcoholated and dealcoholated dimers since our calculation gives rise to the same picture of energy levels in both families of compounds.

The results of this electrostatic calculation do not exclude the occurrence of some kind of electron pair bond between the nickel ions. Obviously, the understanding of the nature of such a bond is a complicated problem that cannot be solved in the context of the calculations presented in this work. The δ–δ interaction found in other nickel dimers (*19*) can also be important in this case and give rise to a bonding ground state, such as a $^3\Sigma_g^-$ or a $^3\Sigma_u^+$, compatible with the observed magnetic moments and a collection of triplet excited states in agreement with the optical spectra. The results of future molecular calculations will greatly contribute to the understanding of this metal–metal interaction as well as clarifying the significance of our present results.

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