the CV process being considered occurs. This is as one would expect for such ligands. Strong evidence for the binuclear Cu^{I}_{2} complex as the product comes from the CV results obtained when $Cu(CH_3CN)_4^+$ and $Na_2(PAA)$ are allowed to react in the electrochemical cell. Sweeping the potential in the positive direction starting from −1.6 V yields a CV wave very similar to the one recorded when sweeping negatively with $Cu_2(PAA)_2$. Thus, the species involved in both cases appear to be the same.

Several conclusions may be drawn from the current study. One is that there are major differences between the redox behavior of the mono- and binuclear complexes and, hence, that the presence of the second metal ion significantly alters the chemical properties. Another is that the electron-transfer properties of these compounds in the absence of simple ions is a reversible, one-electron transfer. However, in the presence of excess simple ions the electron-transfer process consists of two reversible, sequential one-electron transfers with very similar potentials. Finally, there is no significant difference in CV behavior between the bis(1,3,5-triketonato)dicopper(II) complexes and their diamine Schiff-base derivatives except for the absolute value of the redox potentials. In all other aspects the CV waves are superimposable.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE80-10809).

Registry No. $Cu_2(PAA)_2$, 84130-49-4; $Cu_2(PAA)_2en$, 60116-99-6; $Cu_2(PAA)_2$-1,3-pn, 88476-09-9; $CuH_2(PAA)_2en$-N_2O_2, 66745-47-9; $CuH_2(PAA)_2$-1,3-pn-O_2O_2, 88476-10-2; $CuH_2(BAA)_2$-1,3-pn-O_2O_2, 66745-40-2; $Cu_2(BAA)_2$-1,3-pn, 66745-65-1; $Zn_2(PAA)_2$, 88476-11-3; $Cu_2(BAA)_2$, 29745-70-8; $Cu_2(BAA)_2en$, 56550-34-6; Na, 7440-23-5; Li, 7439-93-2.

Supplementary Material Available: Listings of cyclic voltammetric data (6 pages). Ordering information is given on any current masthead page.

Contribution from Chemistry Department I, Inorganic Chemistry,
H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Parametrization of Static Magnetic Susceptibility of a "Linear" Tetranuclear Chromium(III) Complex by Isotropic Heisenberg–Dirac–Van Vleck Hamiltonians and Correlation with Structural Data

TURE DAMHUS† and ERIK PEDERSEN*

Received June 23, 1983

The static magnetic susceptibility of the tetranuclear chromium(III) complex $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]^{6+}$ as a bromide salt, the preparation and X-ray structure of which have been previously reported, has been measured and subjected to interpretation within several different models based on isotropic Heisenberg–Dirac–Van Vleck Hamiltonians with or without biquadratic exchange terms. This has been accomplished with use of new programs that are based on computer diagonalization of such operators because no explicit eigenvalue formulas are known for the linear configuration. The simplest description emerging exhibits two antiferromagnetic couplings, $J_{12} = J_{34} \approx 19$ cm^{-1} and $J_{23} \approx 14$ cm^{-1}, where chromiums 1 and 4 are the terminal ones, and the Hamiltonian is $\sum_{k<l}^{4} J_{kl}\hat{\mathbf{S}}_k\cdot\hat{\mathbf{S}}_l$. The energy levels corresponding to the various parameter sets obtained are presented; the lowest spin multiplets are, in all cases, a ground-state singlet, a triplet at approximately 10 cm^{-1}, and a quintet at approximately 32 cm^{-1}. The parameters of the simplest model are correlated with the structural data by using a generalization of a model recently proposed for corresponding dinuclear complexes.

Introduction

Oligonuclear oxo-, hydroxo- and alkoxo-bridged chromium(III) complexes have become the subject of extensive research in recent years,[1–12] the main effort in work from this laboratory being put into the investigation of correlations between magnetic and structural data for these systems. A model has recently been proposed[9] for such correlations in the dinuclear complexes, and the present work and a related one[4] now give opportunities to investigate extensions of the model to systems with more than two centers. We discuss here the static magnetic susceptibility for the bromide salt $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]Br_6\cdot 2H_2O$, of the particular stereoisomer of a tetrameric cation for which the preparation and structure were reported previously.[10]

Susceptibility data are normally interpreted in terms of just a single model, and the estimated standard deviations for the resultant parameters often seem underestimated. Here we have used two independent data sets and five coupling models and have thereby obtained a broader illustration of the uncertainties involved in deriving the coupling constants and the energies of the spin multiplets.

---

(1) Hodgson, D. J. In "Extended Interactions between Metal Ions in Transition Metal Complexes"; Interrante, L. V., Ed.; American Chemical Society: Washington, DC, 1974; Chapter 9.

(2) Scaringe, R. P.; Hodgson, D. J.; Hatfield, W. E. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 340.

(3) Cline, S. J.; Hodgson, D. J.; Kallesøe, S.; Larsen, S.; Pedersen, E. *Inorg. Chem.* **1983**, *22*, 637–642 and references therein.

(4) Andersen, P.; Damhus, T.; Pedersen, E.; Petersen, A. *Acta Chem. Scand., Ser. A.*, in press.

(5) Damhus, T. Licentiate (Ph.D.) Thesis, University of Copenhagen, 1984, and references therein.

(6) Güdel, H. U.; Hauser, U. *Inorg. Chem.* **1980**, *19*, 1325–1328.

(7) Güdel, H. U.; Hauser, U. *J. Solid State Chem.* **1980**, *35*, 230–239.

(8) Güdel, H. U.; Hauser, U. *Inorg. Chem.* **1979**, *18*, 2730–2737.

(9) Glerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 161–164.

(10) Andersen, P.; Berg, T. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 989–1003. P. Andersen has pointed out that by an unfortunate mistake the configuration of the tetramer is given as ΔΛΔΛ in this paper (abstract and p 1001). It is actually ΔΔΛΛ as is seen in the figures of the paper.

(11) Michelsen, K.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 847–855.

(12) Hauser, U. Inauguraldissertation, Universität Bern, 1979.

† Present address: Department of Pharmaceutical Chemistry AD, Royal Danish School of Pharmacy, DK-2100 Copenhagen Ø, Denmark.

0020-1669/84/1323-0695$01.50/0

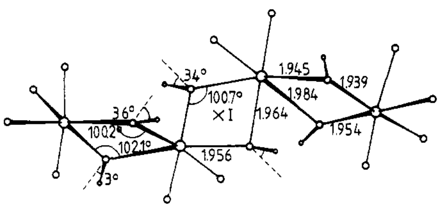

Figure 1. Structure of the cation $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]^{6+}$ as it occurs in the bromide salt discussed in the text. Large circles represent chromium atoms; small circles not in the hydroxo bridges represent the ethylenediamine nitrogens. The molecule has an inversion center at I. We number the chromium atoms 1, 2, 3, 4 proceeding through the chain from one end to the other.

Experimental Section

The static magnetic susceptibility was measured with an instrument based on the Faraday method and partly described elsewhere.[13] The field strength was 12 000 Oe.

The estimated standard deviations $\sigma^2(\chi(T))$ on the susceptibility measurements and $\sigma^2(T)$ on the temperature measurements are reported elsewhere.[11]

Two sets of data were collected, in the following to be denoted I and II. After removal of points that were obviously measurement errors, the full set I consisted of 328 data points with temperatures ranging from 2.4 to 292.2 K, and the full set II consisted of 368 points from 2.2 to 294.2 K.

The Susceptibility Fitting Program

The tetrameric cation under investigation may be schematically represented by Figure 1. The simplest Heisenberg–Dirac–Van Vleck (HDVV) Hamiltonian for this system is

$$\hat{\mathcal{H}} = J\hat{S}_1\cdot\hat{S}_2 + J'\hat{S}_2\cdot\hat{S}_3 + J\hat{S}_3\cdot\hat{S}_4 \qquad (1)$$

where S_1 is the spin on center i and J and J' are exchange coupling constants, all S_i being equal to $^3/_2$. The coefficients to $\hat{S}_1\cdot\hat{S}_2$ and $\hat{S}_3\cdot\hat{S}_4$ have been put equal because of the inversion symmetry of the cation.

For certain other tetrameric systems with some sort of symmetry, discussed in the literature (chromium analogues of Werner's brown salts,[4,6,12] the Pfeiffer and rhodoso ions,[4,7,8,12] and certain corresponding mixed-valence tetranuclear iron complexes[14]), it is possible to rewrite the HDVV Hamiltonian as a linear combination of a set of mutually commuting operators, each of the form $(\hat{S}_{i_1} + \hat{S}_{i_2} + ... + \hat{S}_{i_k})^2$, in such a way that explicit formulas can be given for the eigenvalues of the Hamiltonian in terms of the spin values and the coupling constants. This is not the case for the "linear" system we are considering here, not even for the simple Hamiltonian (1). Thus, to obtain the eigenvalues of (1), one has to set up the matrix of this operator in some suitable basis and diagonalize it. This particular problem formed the impetus for the development in this laboratory of a more general computer program that may set up and diagonalize the matrix of operators

$$\hat{\mathcal{H}} = \sum_{k<l}^{n} [J_{kl}\hat{S}_k\cdot\hat{S}_l + j_{kl}(\hat{S}_k\cdot\hat{S}_l)^2] \qquad (2)$$

for systems with an *arbitrary number of spins* S_k, *arbitrary values of the spins* S_k *on the individual centers, and arbitrary values of the dipolar coupling constants* J_{kl} *and the biquadratic coupling constants* j_{kl}. This energy program forms the basis for another program that may fit an experimental susceptibility curve $(T, \chi^{obsd}(T))$ to the expression

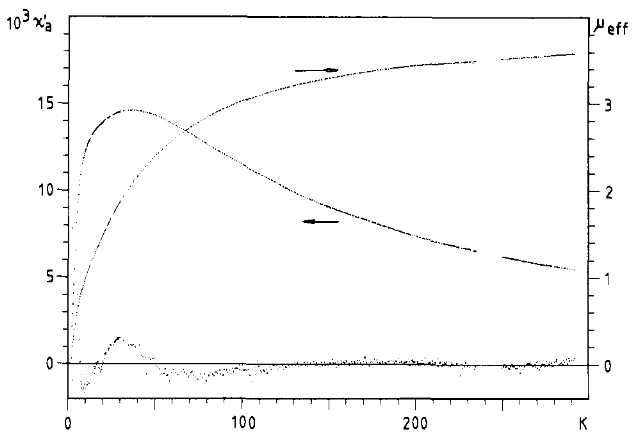

Figure 2. Magnetic susceptibility per chromium (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) of $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]Br_6\cdot2H_2O$. The plot represents those points from 2.4 to 292 K in data set II which were included in the fits to the various models described in the text. The dots distributed closely around the abscissa axis indicate the corresponding values of $(\chi^{obsd} - \chi^{calcd}) \times 20$, where χ^{calcd} refers to the parameters of model 5 in Table II.

Table I. Parameters Used in the Fitting Procedures

model	adjustable parameters	fixed parameters
1	$J_{12} = J_{34}, J_{23}; K$	$g = 1.98; C = 0$
2	$J_{12} = J_{34}, J_{23}; j_{12} = j_{34}, j_{23}; K$	$g = 1.98; C = 0$
3	$J_{12} = J_{34}, J_{23}, J_{13} = J_{24}; j_{12} = j_{34}, j_{23}; K$	$g = 1.98; C = 0$
4	$J_{12} = J_{34}, J_{23}, J_{13} = J_{24}, J_{14}; K$	$g = 1.98; C = 0$
5	$J_{12} = J_{34}, J_{23}; K; C$	$g = 1.98$

$$\chi'(T) = \frac{1}{n}\left[-\frac{N}{H}\,\frac{\sum_i\left(\dfrac{\partial E_i}{\partial H}\right)\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}\right] + \frac{C}{T} + K \qquad (3)$$

by minimization of

$$\sum_j \frac{[\chi^{obsd}(T_j) - \chi'(T_j)]^2}{\sigma^2(\chi(T_j)) + \left[\dfrac{\partial\chi^{obsd}}{\partial T}(T_j)\right]^2\sigma^2(T_j)} \qquad (4)$$

(see the Experimental Section regarding estimated standard deviations). In (3), the E_i values are the energies obtained by diagonalizing (2) with an added isotropic Zeeman term, $\beta gH\cdot\hat{S}$. The adjustable parameters in the fitting procedure are g, the constant C of the Curie term, the additive constant K, the J_{kl}'s, and the j_{kl}'s. Other symbols have their usual meaning. Details on the computer programs are published elsewhere.[4,5]

Results of the Model Fittings

The average magnetic susceptibility per chromium atom and the corresponding effective magnetic moment of a polycrystalline sample of $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]Br_6\cdot2H_2O$ are shown in Figure 2, which is a plot of data set II. Data set I was similar except that the susceptibility curve showed a maximum of 1.48×10^{-2} cgsu at a temperature of 35 K rather than a maximum of 1.46×10^{-2} cgsu at 37 K. Tables II and III show the results of fitting the

---

(13) Josephsen, J.; Pedersen, E. *Inorg. Chem.* **1977**, *16*, 2534–2538 and references therein.

(14) Papaefthymiou, G. C.; Laskowski, E. J.; Frota-Pessôa, S.; Frankel, R. B.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 1723–1728.

Table II. Parameters Derived from Magnetic Susceptibility Data in the Temperature Range 8.5–292 K

	fitted parameters[b]	
	data set I	data set II
	Model 1[a]	
K, cgsu	$1.9\ (1) \times 10^{-5}$	$-2.5\ (1) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	18.842 (3)	19.047 (3)
J_{23}, cm^{-1}	14.91 (2)	14.29 (2)
var/f[c]	1.12	1.29
	Model 2	
K, cgsu	$1.3\ (1) \times 10^{-5}$	$-2.0\ (2) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	19.64 (6)	19.41 (5)
J_{23}, cm^{-1}	13.4 (2)	14.1 (1)
$j_{12} = j_{34}$, cm^{-1}	0.24 (2)	0.11 (2)
j_{23}, cm^{-1}	0.34 (6)	0.43 (6)
var/f	0.87	1.12
	Model 3	
K, cgsu	$7\ (3) \times 10^{-6}$	$-2.9\ (2) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	17.3 (3)	19.5 (1)
J_{23}, cm^{-1}	16 (1)	19 (1)
$J_{13} = J_{24}$, cm^{-1}	−0.4 (5)	−2.1 (4)
$j_{12} = j_{34}$, cm^{-1}	−0.51 (6)	0.28 (1)
j_{23}, cm^{-1}	−1.5 (2)	2.1 (2)
var/f	0.87	0.97
	Model 4	
K, cgsu	$1.6\ (2) \times 10^{-5}$	$-2.6\ (2) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	17.3 (1)	19.59 (8)
J_{23}, cm^{-1}	19.3 (4)	12.6 (1)
$J_{13} = J_{24}$, cm^{-1}	−1.5 (1)	0.56 (6)
J_{14}, cm^{-1}	1.3 (1)	−0.7 (1)
var/f	0.97	1.11

[a] See Table I for definition of the models. [b] Standard deviations on last digit in parentheses. [c] Variance per degree of freedom.

Table III. Parameters Derived from Magnetic Susceptibility Data in the Temperature Range 2.4–292 K

	fitted parameters	
	data set I	data set II
	Model 1	
K, cgsu	$2.5\ (4) \times 10^{-6}$	$-1.2\ (5) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	18.83 (1)	19.06 (2)
J_{23}, cm^{-1}	15.17 (7)	14.60 (9)
var/f	17.34	33.40
	Model 2	
K, cgsu	$4.6\ (6) \times 10^{-5}$	$+2.5\ (7) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	19.6 (2)	19.5 (2)
J_{23}, cm^{-1}	15.6 (5)	16.7 (5)
$j_{12} = j_{34}$, cm^{-1}	0.25 (6)	0.16 (7)
j_{23}, cm^{-1}	1.6 (3)	2.0 (3)
var/f	15.15	29.35
	Model 5	
C, cgsu K	$7.8\ (3) \times 10^{-3}$	$+3.65\ (7) \times 10^{-3}$
K, cgsu	$-2.6\ (3) \times 10^{-5}$	$-4.5\ (2) \times 10^{-5}$
$J_{12} = J_{34}$, cm^{-1}	19.23 (2)	19.216 (7)
J_{23}, cm^{-1}	13.67 (7)	13.79 (3)
var/f	5.93	4.05

models of Table I to the susceptibility data.

We preface the discussion of these models by the following two remarks.

First, the bromide salt described in ref 10 was analyzed to 4 H_2O of crystallization whereas the subsequent X-ray structure showed only 2 H_2O. To ensure that a correct molar weight was used for the sample at the time of the susceptibility measurements, some preliminary fits were performed in which the molar weight was varied (by varying a multiplicative constant in front of the susceptibility expression (3)) in addition to $J_{12} = J_{34}$, J_{23}, and K. For both data sets a molar weight consistent with 2 H_2O was obtained in this way with use of data in the temperature range 8.5–292 K (although it was strongly correlated with the other parameters), and this molar weight was then fixed in all subsequent calculations.

Second, the program allows, as already mentioned, for a variable g factor. Several preliminary fits were tried with g variable. As a general experience, g was strongly correlated with one or several of the other parameters, especially the additive constant K. The runs with data from 8.5 to 292 K and $J_{12} = J_{34}$, J_{23}, K, and g variable gave a g factor of 1.981 (1) for data set I and 1.980 (1) for data set II. Including more parameters or extending the temperature range to 2.4–292 K gave variations in g of up to 0.03 away from 1.98 and very strong correlations. On this background, a fixed g value of 1.98 was chosen for all the final fittings.

Models 1 and 2 include only neighbor interactions in the chain of four chromium(III) centers while models 3 and 4 include some or other more distant interactions. Models 2, 3, and 4 all give better fits than model 1 (as measured by the variance per degree of freedom, var/f). However, model 3 leads to unacceptably high standard deviations, and 3 and 4 are both heavily correlated models. Model 2 is equally acceptable as models 3 and 4 from a var/f point of view, at least for data set I; it furthermore gives reasonable standard deviations, and only J_{12} and j_{12} are seriously correlated (i.e. have a correlation coefficient numerically exceeding 0.8). The variance matrix for model 1 is very satisfactory. Thus, we shall concentrate now on models 1 and 2.

Since it is reasonable to expect coupling constants, J_{kl} and j_{kl}, to be—in principle—temperature dependent, it seemed desirable to try out models 1 and 2 also on data from a more narrow temperature range. We thus repeated the fitting for data only from 8.5 to 150 K. Model 1 is very stable to this restriction of data, the coupling constants remaining unchanged to within 0.1 cm^{-1} and K changing at most 1×10^{-5} cgsu. In model 2, especially K is somewhat more sensitive and becomes more correlated with other parameters, but still both types of coupling constants only change within few tenths of a cm^{-1}. var/f is in all cases larger than for the complete data set.

Another relevant experiment was to include the low-temperature data from 2.4 to 8.5 K. This again resulted in only small changes in the coupling constants for model 1 and moderate changes for model 2, the middle couplings, J_{23} and j_{23}, being the more sensitive (Table III). However, var/f went up drastically. Since even minute amounts of an admixed substance following a Curie law (e.g., monomer impurities) could be suspected to have influence on the fitting to the low-temperature data, it was decided to run one further model varying the constant C in eq 3; model 5 of Table I was chosen.

As is seen from Table III, the fit is substantially improved by the introduction of the Curie term. The magnitude of C corresponds to the presence of some 0.2–0.4% "monomer" with $\mu_{eff} = 3.8\ \mu_B$. Furthermore, if model 1 is modified by taking the C values from Table III instead of $C = 0$ and is then fitted to the data from 8.5 to 292 K, the parameters K, $J_{12} = J_{34}$, and J_{23} remain virtually unchanged, the differences from the model 5 values given in Table III being less than 2 standard deviations. On the other hand, the fits in this temperature range become poorer than the model 1 fits in Table II (var/f = 4.41 for data set I, var/f = 2.24 for data set II). Furthermore, as is seen from Figure 2, the largest contribution to var/f in model 5 (Table III) still comes from the low-temperature data. Thus, the introduction of a Curie term to fit the low-temperature data should probably be regarded with some caution. Since the influence on the coupling constants—which are our main concern here—is only of the order of magnitude of 1 cm^{-1} and often less, we shall not pursue this aspect further.

Correlation with Structural Data

Recently, a model was proposed[9,15] that relates the dipolar

Table IV. Energies (cm^{-1}) of the Lowest 10 Spin Multiplets with Parameters As Fitted to Some of the Models of Tables II and III[c]

model 1		model 2	model 5
data set I[a]	data set II[a]	data set II[a]	data set II[b]
(0) 0	(0) 0	(0) 0	(0) 0
(1) 9.6	(1) 9.8	(1) 9.8	(1) 10.0
(2) 32.2	(2) 32.8	(2) 33.1	(2) 33.5
(1) 46.3	(1) 45.0	(1) 42.7	(1) 44.1
(1) 50.7	(1) 50.3	(1) 47.8	(1) 49.8
(2) 64.1	(0) 63.5	(2) 61.9	(0) 61.9
(0) 65.0	(2) 64.0	(0) 62.0	(2) 64.0
(3) 70.2	(3) 71.2	(3) 71.1	(3) 72.0
(2) 76.0	(2) 76.1	(2) 74.4	(2) 76.0
(1) 84.9	(1) 84.7	(1) 83.0	(1) 84.5

[a] Data in the range 8.5–292 K. [b] Data in the range 2.4–292 K. [c] Numbers in parentheses are values of the total spin.

coupling constant in a symmetrical doubly hydroxo-bridged chromium(III) dimer to structural parameters for the bridging moiety.

We shall investigate here to what extent the model works if it is extended to the linear tetramer, considering this ion as composed of three dimer fragments.

The molecular structure of the tetranuclear cation as it occurs in the bromide salt under discussion here was reported in ref 10 based on a room-temperature single-crystal X-ray structure. The details relevant for our present purposes are given in Figure 1. As is seen, the dimer moieties are not exactly symmetrical. To be able to apply the model of ref 9, we idealize them by averaging the bond lengths and angles.[16] This gives r = 1.955 (4) Å, φ = 101.2 (2)°, and θ = 19.6 (70)° for the end fragment and r = 1.960 (4) Å, φ = 100.7 (2)°, and θ = 33.6 (70)° for the central fragment. Applying the model referred to above, we get the following values for the coupling constants:

$$J_{12}(\text{model}) = 21.6\ (17)\ \text{cm}^{-1}$$

$$J_{23}(\text{model}) = 15.5\ (27)\ \text{cm}^{-1}$$

We have given in parentheses the variation of J values obtained by varying θ by 1 standard deviation on either side of the above values; among the three structural parameters, θ is the only one whose standard deviation gives rise to variations in the J values exceeding the standard deviations estimated in the fitting procedures. The model J values arise as 21.6 = 27.2 − 5.6 and 15.5 = 20.6 − 5.1 (antiferromagnetic contribution plus ferromagnetic contribution).

We see that all coupling constants arrived at with the use of models 1 and 5 agree with J_{12}(model) and J_{23}(model) within 2 standard deviations.

Energies of the Lowest Spin Multiplets

For all the parameter sets reported in Tables II and III, the energies of the Hamiltonian (2) have been calculated. All parameter sets indicate that the three lowest spin multiplets are a singlet, a triplet at 9.8 ± 0.2 cm^{-1}, and a quintet around 32 cm^{-1}. Some sample energy calculations are given in Table IV. Except for the three lowest spin multiplets, the energies calculated by the use of model 4 deviate considerably from the ones given in Table IV.

For models 1 and 5, the energy spectrum may be further discussed by reference to Figure 3, which was constructed by repeated diagonalization of the Hamiltonian (1). The abscissa here is the ratio $\alpha = J_{23}/J_{12}$, and the ordinate is the energy of the various spin multiplets in units of J_{12}. If the standard deviations are taken into account, the model 1 data of Table II give α values between 0.790 and 0.793 (data set I) and between 0.749 and 0.751 (data set II) while the model 5 data of Table III give α values between 0.706 and 0.715 (data set I) and between 0.716 and 0.719 (data set II). Inspection of Figure 3 shows that the energies of the five lowest spin multiplets are very stable within the range α = 0.7–0.8, while the next to lowest singlet and quintet have a crossing point in this interval, as also evidenced by Table IV.

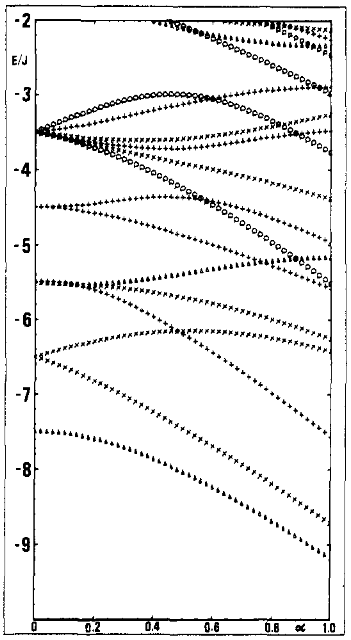

Figure 3. Partial energy diagram (energies up to −2 J) of the Hamiltonian (1) in units of J and as a function of $\alpha = J'/J$. Designations for values of the total spin: (△) singlet; (×) triplet; (+) quintet; (○) septet.

Part of Figure 3 has been given in ref 17 in a different context.

Further plots similar to Figure 3, but covering the whole range of possible ratios J_{23}/J_{12} from −∞ to ∞, have been produced[5] and are available from the authors upon request. They show that for J_{12} and J_{23} both positive (i.e., both couplings antiferromagnetic), the lowest multiplet is always a singlet.

Conclusions

A new general and flexible program has enabled a thorough analysis of several parametrizations, based on isotropic HDVV spin-coupling Hamiltonians, of the magnetic susceptibility of a bromide salt of the tetranuclear chromium(III) complex under discussion here. The data are described very well by the simple Hamiltonian (1) with $J \approx 19$ cm^{-1} and $J' \approx 14$ cm^{-1}, and these values fit nicely with the predictions of the GHP model[9] on the basis of the room-temperature X-ray structure. Further improvement of the susceptibility fit may be obtained by adding biquadratic terms for the 1 ↔ 2, 2 ↔ 3, and 3 ↔ 4 interactions and/or allowing more distant interactions within the chain. The former type of amendment works rather satisfactorily, but including non-neighbor interactions gives heavy correlations and parameters with large standard deviations. All parameter sets indicate a singlet as the lowest spin multiplet with a triplet at about 10 cm^{-1} and a quintet at around 32 cm^{-1}.

---

(15) Damhus, T. *Mol. Phys.* **1983**, *50*, 497–513.

(16) In connection with the trinuclear complex described in ref 4, *separate* calculations were made of the contributions from the two parts of a nonsymmetrical dihydroxo bridge. The final result did not differ significantly, however, from that obtained by using average values of angles and bond lengths.

(17) Güdel, H. U.; Hauser, U. *Theor. Chim. Acta* **1983**, *62*, 319–327.

Acknowledgment. The authors wish to thank Dr. Peter Andersen for supplying a sample of the tetranuclear chromium complex and Solveig Kallesøe for performing the measurements. This work was supported by the Danish Natural Science Research Council through Grant Nos. 511-20608, 11-2205, and 11-3296 (to T.D.) and Grant Nos. 511-742, 511-3993, and 511-10576 (to E.P.).

Registry No. $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]Br_6$, 69831-99-8.

Contribution from the Chemistry Department and Energy and Mineral Resources Research Institute,
Iowa State University, Ames, Iowa 50011

Polarized Electronic Absorption Spectra of Dichlorotetrakis(μ-pivalato)dirhenium(III)

DON S. MARTIN,* HAI-WEI HUANG, and ROBERT A. NEWMAN

Received June 2, 1983

Single-crystal polarized absorption spectra are reported for $Re_2[O_2CC(CH_3)_3]_4Cl_2$ from 15 000 to 35 000 cm^{-1}. A peak at 20 600 cm^{-1} with molecular z polarization is assigned as the electric-dipole-allowed $^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition. A much weaker band at 16 500 cm^{-1} with x,y polarization can be the spin-forbidden $^1A_{1g} \rightarrow {}^3A_{2u}$ ($\delta \rightarrow \delta^*$) transition. Weak transitions are observed at 21 600, 24 700, 29 000, and 32 000 cm^{-1}. They appear to be electric-dipole-forbidden, vibronically allowed transitions. Their possible assignments are discussed.

Introduction

The dimeric complexes of molybdenum(II) and rhenium(III) possess the unusual quadruple bond between the transition-metal atoms. Recent theoretical treatments of these systems[1-6] have generally indicated that the lowest energy electronic excitation in such dimers should be $\delta \rightarrow \delta^*$ transitions. Many of these dimers have four ligands with square-planar coordination of the bonds to each metal atom. With an eclipsed configuration of equivalent bonds the dimers possess a local D_{4h} symmetry. The $\delta \rightarrow \delta^*$ transition can then be characterized as $A_{1g} \rightarrow A_{2u}$ ($b_{1g} \rightarrow b_{2u}$). Such a singlet–singlet transition $^1A_{1g} \rightarrow {}^1A_{2u}$ should be electric dipole allowed for light polarized along the molecular z axis, which lies along the metal–metal bond. Single-crystal polarized optical spectroscopy therefore offers the possibility of a definitive identification of this transition. From crystal spectra for the tetrabutylammonium salts of octachloro- and octabromodirhenate(III), Cowman and Gray,[7] Cowman et al.,[8] and Trogler et al.[9] have demonstrated that the polarization for the electronic band observed at the lowest energy in single crystals was consistent with the $\delta \rightarrow \delta^*$ assignment. Fanwick et al.[10] similarly showed that the lowest energy observed band in $K_4Mo_2Cl_8{\cdot}2H_2O$ possessed the z polarization and assigned the band as the spin-allowed $\delta \rightarrow \delta^*$ transition. The polarized spectra for $K_4Mo_2(SO_4)_4{\cdot}2H_2O$, which contains the $Mo_2(SO_4)_4{}^{4-}$ dimeric ion with four bridging sulfates, also indicated that the lowest electronic band had the z polarization expected for the $\delta \rightarrow \delta^*$ polarization.[11]

A number of polarized single-crystal spectra for compounds with tetrakis(μ-carboxylato)dimolybdenum(II) complexes have presented a more puzzling situation for the lowest energy absorption band. Crystals of these compounds have provided highly resolved, unusually rich vibrational structures for the band at liquid-helium temperatures. Vibrational lines with comparable intensities were observed that had strikingly different polarization ratios so overwhelming intensity could not be assigned to a z polarization as expected for a normal dipole-allowed transition, $^1A_{1g} \rightarrow {}^1A_{2u}$. The spectra have frequently been compromised by the low crystal site symmetries and by the presence of defect components. However, from the orientation of the transition moment and hot bands observed for crystals of dimolybdenum tetraacetate[14] it is demonstrated that the band was electric dipole allowed for molecular z polarization, but the transition moment was so low that vibronically excited lines contributed a substantial intensity to the band. Single-crystal spectra for a tetrakis(carboxylato)-bridged rhenium(III) complex have not been reported previously because of the difficulty of preparing suitable crystalline specimens, resulting from the low solubility of the compounds in convenient solvents. The present study provides the spectra for such a dimer, viz., $Re_2[O_2CC(CH_3)_3]_4Cl_2$.

Experimental Section

The compound was prepared by the procedure of Collins, Cotton, and Gage.[15] They reported from an X-ray diffraction study the crystal structure with a tetragonal cell, $I4/m$, $Z = 2$, $a{:}c$ = 11.469 (4):10.733

---

(1) Norman, J. G., Jr.; Kolari, H. J. *J. Chem. Soc., Chem. Commun.* **1975**, 649.

(2) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 33.

(3) Mortola, A. P.; Moscowitz, J. W.; Rosh, N.; Cowman, C. D.; Gray, H. B. *Chem. Phys. Lett.* **1975**, *32*, 283.

(4) Noodleman, L.; Norman, J. G., Jr. *J. Chem. Phys.* **1979**, *70*, 4903.

(5) Norman, J. G., Jr.,; Ryan, J. B. *J. Comput. Chem.* **1980**, *1*, 59.

(6) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2897.

(7) Cowman, C. D.; Gray, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8177.

(8) Cowman, C. D.; Trogler, W. C.; Gray, H. B. *Isr. J. Chem.* **1967/77**, *15*, 308.

(9) Trogler, W. C.; Cowman, C. D.; Gray, H. B.; Cotton, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 2993.

(10) Fanwick, P. E.; Martin, D. S.; Cotton, F. A.; Webb, T. R. *Inorg. Chem.* **1977**, *16*, 2103.

(11) Cotton, F. A.; Martin, D. S.; Fanwick, P. E.; Peters, T. J.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 4681.

(12) Cotton, F. A.; Martin, D. S.; Webb, R. R.; Peters, T. J. *Inorg. Chem.* **1976**, *15*, 1199.

(13) Trogler, W. C.; Solomon, E. I.; Trajberg, I.; Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1977**, *16*, 828.

(14) Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2511.

(15) Collins, D. M.; Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1712.