Journal of Organometallic Chemistry, 101 (1975) 321—330

THE MAGNETIC PROPERTIES OF THE DIMERIC VANADIUM(III) COMPLEXES TETRA-μ-CARBOXYLATOBIS[π-CYCLOPENTADIENYL-VANADIUM(III)] FOR R = METHYL, PHENYL AND FURANYL GROUPS

KENNETH T. McGREGOR*, VLADIMIR T. KALINNIKOV**
and WILLIAM E. HATFIELD*

Department of Chemistry, University of North Carolina, Chapel Hill,
North Carolina 27514 (U.S.A.)

(Received May 30th, 1975)

Summary

Magnetic susceptibilities have been measured in the temperature range 113-370 K for the dimeric compounds tetra-μ-carboxylatobis[π-cyclopentadienylvanadium(III)] for R = methyl, phenyl and furanyl groups. The $S = 1$ vanadium(III) ions are exchange coupled with coupling constants of —227, —197, and —185 cm^{-1}, respectively. The corresponding biquadratic coupling constants are 17, 34, and 36.5 cm^{-1}, respectively. The EPR spectra also reflect the exchange coupling.

Introduction

Many polynuclear transition metal complexes formed with bridging carboxylate groups have been found to exhibit very interesting magnetic properties due to exchange interactions between the metal centers. Although several different metal systems have been studied, the most extensive characterization has been given to copper(II) complexes [1]. The well known dimeric complex copper acetate monohydrate $Cu_2Ac_4 \cdot 2H_2O$ is the most prominate example [2]. The large exchange interaction found in $Cu_2Ac_4 \cdot 2H_2O$ has been attributed to both direct exchange by weak copper—copper bonding and to superexchange via the acetate bridges. The relatively short copper—copper separation [3] of 2.614 Å does not rule out the former premise.

Recently, the preparation and magnetic moments for a series of vanadium(III) carboxylate complexes of the type $[CpV(OOCR)_2]_2$ (Cp = π-cyclopentadiene) were reported [4]. Here R can be a variety of substitutional groups, both aliphat-

---

[*] Present address: Department of Chemistry, Princeton University, Princeton, New Jersey 08540.

[**] Present address: N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, Moskow W-71, (U.S.S.R.)

ic and aromatic. The crystal and molecular structures of two of the members of this series have been determined [5,6]. The structural investigations reveal the complexes to be dimeric with the V^{III} ions bridged by four carboxylate groups. The vanadium—vanadium separation was found to be ~3.7 Å which precludes any vanadium—vanadium bonding. However, the subnormal magnetic moments exhibited by these complexes are suggestive of substantial interactions between the vanadium centers.

In order to characterize fully the nature and magnitude of the interactions present in these systems, we have undertaken magnetic susceptibility and electron paramagnetic resonance studies of three members of this series. The results of our investigations for R = CH_3, C_6H_5, and C_4H_3O are reported herein.

Experimental

The $[CpV(OOCR)_2]_2$ complexes were prepared as previously reported [4].

The magnetic susceptibilities of the complexes, in the temperature range 77-375 K, were measured by the Faraday method [7], using a Cahn electrobalance equipped with a digital voltmeter. A sample of $Hg[Co(SCN)_4]$ was used to calibrate the balance [8]. The data were corrected for the diamagnetism of the constituent atoms using Pascal's constants [9].

EPR spectra of powdered samples were recorded at 4.2, 77, and 295 K with a Varian 4502 spectrometer. Spectra were also recorded, in the temperature range 100-295 K, with a JEOL-ME-3X spectrometer equipped with a JES VT-3 temperature controller. All spectra were obtained with X-band microwave frequencies and 100 kHz magnetic field modulation. The spectra shown correspond to a microwave frequency of 9.39 GHz. A Magnion 502 Precision Gaussmeter and a Hewlett—Packard 5245L frequency counter were used to calibrate the magnetic field strengths and microwave frequencies. All temperature measurements were made with a calibrated Ga/As diode.

Results

The magnetic susceptibility data collected for the three complexes are given in Table 1. The magnetic data are displayed as the effective magnetic moment, $\mu_{eff}(= 2.83[\chi_m T]^{1/2})$. The temperature variation of μ_{eff} for the benzoate complex is shown in Fig. 1 along with some calculated curves (vide post). The temperature dependence of μ_{eff} seen in Fig. 1 is representative of all three complexes.

The 295 K EPR spectrum of the benzoate complex is shown in Fig. 2. As seen from Fig. 2, a very broad and intense resonance is centered at ~3400 G with distinct shoulders on either side of the central peak. This absorption spans the 2500-4200 G region of the spectrum. Resonances are also found at ~1700 G and ~1100 G. The 295, 162, and 100 K spectra of the acetate complex are shown in Fig. 3. These spectra are very similar to the benzoate complex although the total width of the resonances are slightly smaller. The spectra of the furan complex are also similar to Figs. 2 and 3. However, the resonance widths are more narrow than the acetate complex and the shoulders are barely resolved. The temperature dependence of the full-field spectra of the acetate and furan

TABLE 1

OBSERVED MAGNETIC PROPERTIES FOR $[CpV(OOCR)_3]_2$

$R = C_4H_3O$		$R = CH_3$		$R = C_6H_5$	
T (K)	μ_{eff} (B.M.)	*T* (K)	μ_{eff} (B.M.)	*T* (K)	μ_{eff} (B.M.)
190	1.14	113	0.62	113	0.57
231	1.32	190	1.05	154	0.81
~~250~~	~~1.43~~	~~226~~	~~1.26~~	~~195~~	~~1.06~~
273	1.54	273	1.46	228	1.25
296	1.63	296	1.56	250	1.38
297	1.64	301	1.58	273	1.51
305	1.67	305	1.60	296	1.59
315	1.70	310	1.63	296	1.56
325	1.74	315	1.64	305	1.63
335	1.78	325	1.68	315	1.67
345	1.81	335	1.71	325	1.71
355	1.85	346	1.74	335	1.75
365	1.87	356	1.76	345	1.78
375	1.91			355	1.81
				365	1.84

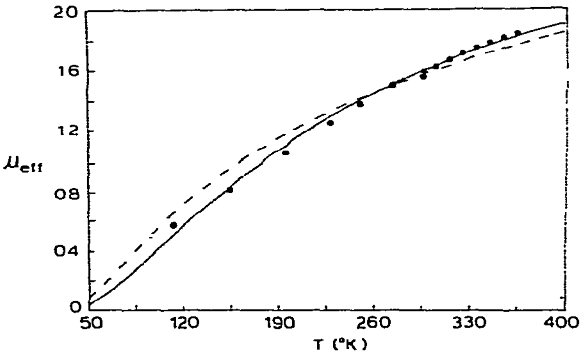

Fig. 1. The temperature variation of the effective moment for the benzoate complex. The solid curves were generated with eqn. 6 (see text).

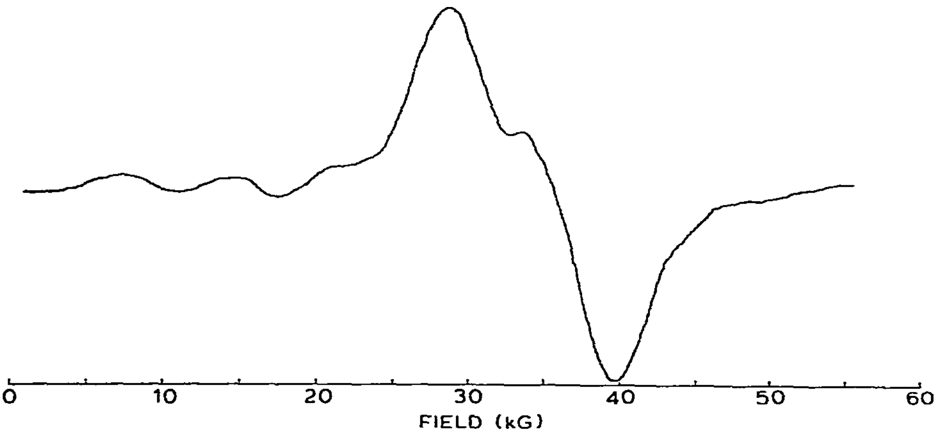

Fig. 2. The 295 K EPR spectrum of the benzoate complex. The spectrum corresponds to a microwave frequency of 9.39 GHz.

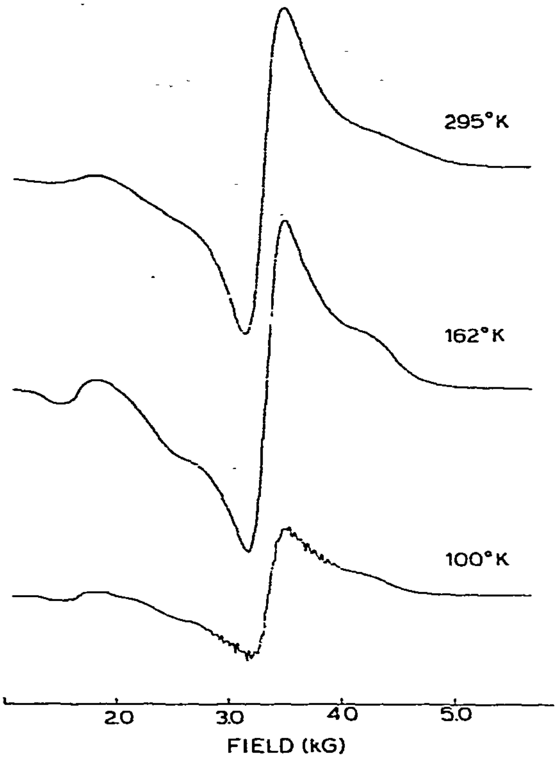

Fig. 3. The temperature dependence of the full-field EPR spectrum of the acetate complex.

analogs are very similar. At 77 K, the spectra resemble the 100 K trace seen in Fig. 3. At this temperature the partial resolution of additional structure is observed. The full-field 77 K spectrum of the benzoate analog reveals a host of resonance lines which appear to result from a small amount of paramagnetic impurity which supports superhyperfine structure. A monomeric vanadyl ($S = 1/2$) species is suspected to be the impurity. This supposition is supported by the 4.2 K spectrum which reveals 8 intense hyperfine lines with additional superhyperfine structure. The additional lines observed at 77 K are absent as well as the half-field resonances.

The half-field 77 K spectra of the acetate and benzoate complexes are shown in Fig. 4a and 4b, respectively. The corresponding spectrum of the furan complex is identical to the benzoate spectrum. The half-field spectra of the acetate complex, in the 111-162 K temperature range, are shown in Fig. 5. The temperature dependence of these spectra is representative of all the complexes.

Discussion

The magnetic properties described above can be understood by considering the V^{III} pairs to be exchange coupled according to the spin Hamiltonian (eqn. 1):

$$H = H^1 + H^2 + H^{ss} \qquad (1)$$

where the H^i ($i = 1,2$) describe the magnetic interactions of the single ions of

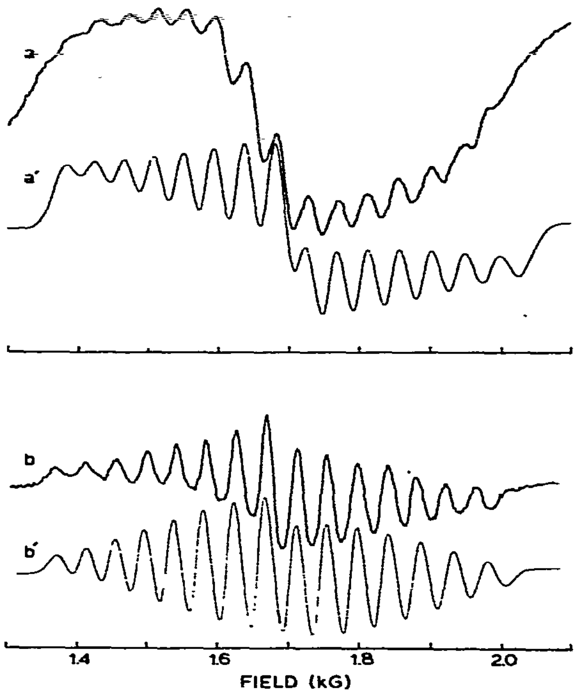

Fig. 4. The experimental and calculated spectra of the $[CpV(OOCR)_2]_2$ complexes: (a) the acetate complex and (b) the benzoate complex. The spectra were recorded at 77 K with $\nu = 9.39$ GHz.

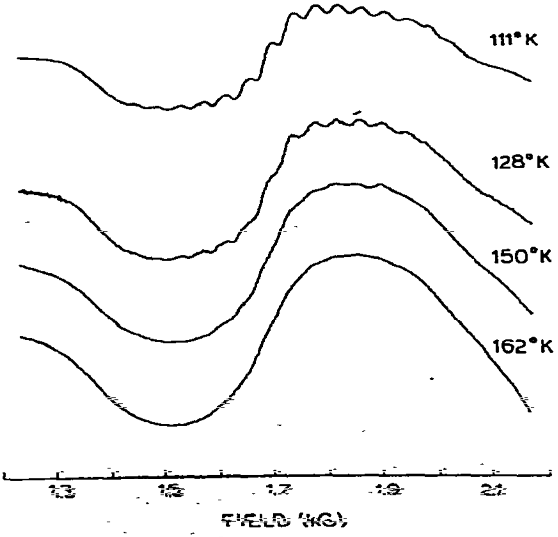

Fig. 5. The temperature dependence of the half-field spectrum of the acetate complex.

the pair and H^{ss} accounts for the interactions between the single ions. The single ion Hamiltonians have the form shown in eqn. 2 [10]

$$H^i = \beta \underline{S}^i \cdot \underline{\underline{g}}^i \cdot \underline{H}^i + \underline{S}^i \cdot \underline{\underline{A}}^i \cdot I^i + D^i[3(S^i_z)^2 + \tfrac{1}{3}S^i(S^i+1)] + E^i[(S^i_x)^2 - (S^i_y)^2] \qquad (2)$$

where the terms have their usual meanings. The Hamiltonian given in eqn. 3 is usually sufficient [10-12] to account for the pairwise interaction between the single ions.

$$H^{ss} = \underline{S}^i \cdot \underline{\underline{D}}^e \cdot \underline{S}^j - J\underline{S}^i \cdot \underline{S}^j - j(\underline{S}^i \cdot \underline{S}^j)^2 \qquad (3)$$

In eqn. 3, the D^e-tensor accounts for the dipolar and anisotropic exchange interactions between the ions while J and j represent the bilinear and biquadratic isotropic exchange parameters, respectively. In order to analyze the observed magnetic properties of the complexes, it is convenient to transform the Hamiltonian (eqn. 1) into the total spin representation $S = S^i + S^j$ as given [11,12] by eqn. 4.

$$\begin{aligned} H = {} & \beta \underline{S} \cdot \underline{\underline{g}} \cdot \underline{H} + (1/2)\underline{S} \cdot (\underline{\underline{A}}^i \cdot I^i + \underline{\underline{A}}^j \cdot I^j) + D[S_z^2 - \tfrac{1}{3}S(S+1)] \\ & + E(S_x^2 - S_y^2) - (J/2)[S(S+1) - S^i(S^i+1) - S^j(S^j+1)] \\ & - (j/4)[S(S+1) - S^i(S^i+1) - S^j(S^j+1)]^2 \end{aligned} \qquad (4)$$

Here the zero-field term D is composed of both single ion $\underline{\underline{D}}^i$ and $\underline{\underline{D}}^e$ contributions as given by eqn. 5 [12].

$$D = 3\alpha_s D^e + \beta_s D^i \qquad (5)$$

where $\alpha_s = \frac{1}{2}\,\frac{S(S+1) + 4S^i(S^i+1)}{(2S-1)(2S+3)}$ and $\beta_s = \frac{3S(S+1) - 3 - 4S^i(S^i+1)}{(2S-1)(2S+3)}$.

Here, D^e is defined as $(3/2)D^e_z$. The rhombic term E is given by similar expressions; however, this term is expected to be very small and will be neglected here. Moreover, the polycrystalline data are probably not sufficient to evaluate this term if present. The bilinear isotropic exchange interaction in eqn. 4 leads to total spin states with $S = 0$, 1 and 2 for the $S^i = S^j = 1$ vanadium(III) ($3d^2$) case. The energies E_S of the singlet, triplet, and quintet states are 0, $-J$, and $-3J$, respectively. The biquadratic interaction shifts the levels to give: $E_0 = 0$, $E_1 = -J + 3j$, $E_2 = -3J + 3j$, where we have assigned the zero of energy to the singlet state. By neglecting the fine and hyperfine terms in eqn. 4 and assuming a Boltzmann distribution for the thermal population of the states, the magnetic susceptibility of the vanadium(III) pairs (per V^{III} ion) is given by eqn. 6.

$$\chi_m = \frac{Ng^2\beta^2}{kT}\,\frac{5 + \exp(-2J/kT)}{5 + 3\exp(-2J/kT) + \exp[(-3J+3j)/kT]} \qquad (6)$$

The curves shown in Fig. 1 represent the best least squares fit of the effective moment calculated from eqn. 6 to the observed moments. The dashed curve represents the best fit in the absence of biquadratic exchange while the full curve depicts the best fit including the biquadratic term. The least squares routine used for the fitting minimizes the function: $F = \Sigma(\mu_{obs} - \mu_{calc})^2/\Sigma\mu_{obs}$ as the criterion for the best fit. In order to limit the number of parameters to be determined, the EPR

g-values (see below) were used for the fitting. The exchange parameters derived from eqn. 6 are given in Table 2.

The relatively large exchange parameters indicated by the bulk magnetic data are consistent with the observed EPR spectra. The temperature dependence of the spectra can also be understood in terms of a Boltzmann distribution for the population of the states. The densities ρ_s of the thermally populated excited states are given by eqn. 7.

$$\rho_s = \rho_0 g_s \exp(-E_s/kT) \qquad (7)$$

where $\rho_0 = [1 + \Sigma g_s \exp(-E_s/kT]^{-1}$.
Here, ρ_s represents the triplet or quintet densities, ρ_0 is the ground state density, and g_s is the degeneracy of the state S. For an exchange parameter of 250 cm^{-1} the triplet state is ~44% populated and the quintet state is ~6.3% at ambient temperatures. At 77 K, ~3% of the ion pairs are in triplet states while the quintet state is infinitesimally populated. Therefore, according to eqn. 7, at 295 K observation of resonances within the multiplets of both magnetic states are possible, however, at 77 K only transitions of the triplet state can be observed.

For the present systems (see Fig. 1), it is likely that the full-field spectra measured at 295 K are due to the $\Delta M_s = 1$ transitions of both magnetic states. Similarly, the half-field absorption could contain the $\Delta M_s = 2$ transitions of both states while the third-field absorption is due to the $\Delta M_s = 3$ transitions within the quintet state only. Since the spectra observed at 77 K arise from the transitions within the $S = 1$ multiplet only, these spectra may be used to derive the magnetic parameters of the triplet state; these parameters may then be related to the other parameters of the Hamiltonian. In the determination of the triplet state parameters, the half-field spectra are the most useful since the hyperfine structure is well resolved. The computer simulations of these spectra are shown in Fig. 4a′ and 4b′. The simulations assume that all of the interactions have the same coordinate systems and accounts for the powder average of the spectra [13,14]. The parameters derived from the simulations are listed in Table 3. The hyperfine interaction was found to be isotropic within the sensitivity of measurement. Although, the g-values and hyperfine coupling constants derived from the half-field spectra are thought to be reasonably accurate, a large uncertainty is associated with the value of D since the $\Delta M_s = 2$ transitions are somewhat insensitive to the zero-field splitting.

By using eqn. 5 to evaluate the zero-field parameters of the different multiplets and using eqn. 4 to generate the spectra, both the triplet and quintet resonances would be observed in the 2500-4500 G region for a single ion zero-field

TABLE 2

EXCHANGE PARAMETERS FOR [CpV(OOCR)$_2$]$_2$

	$j = 0$		$j \neq 0$			
R	J(cm^{-1})	F(× 10^4)	J(cm^{-1})	j(cm^{-1})	F(× 10^4)	j/J
CH_3	−255	9.5	−227	17	3.6	0.075
C_6H_5	−252	34	−197	34	5.2	0.172
C_4H_3O	−235	11	−185	36.5	1.1	0.197

TABLE 3

TRIPLET STATE EPR PARAMETERS FOR $[CpV(OOR)_2]_2$

R	g_z(± 0.01)	g_{xy}(± 0.01)	A(± 5)(× 10^4) (cm^{-1})	D(± 0.005) (cm^{-1})
CH_3	2.00	1.95	80 (5)	0.05
C_6H_5	1.97	1.99	80 (5)	0.04
C_4H_3O	1.97	1.99	80 (5)	0.04

splitting of ~0.05 cm^{-1}. Here we have assumed a dipolar-only value for D^e, based on the V^{III}—V^{III} separation [5], of 0.055 cm^{-1}. These parameters are consistent with the half-field simulations.

The temperature dependence of the spectra seen in Figs. 3 and 5 is consistent with the state densities given by eqn. 7. Most notably, the $\Delta M_s = 3$ transitions which arise from population of the quintet state are absent in the lower temperature spectra. Also, as seen from Fig. 5, as the temperature increases the hyperfine lines broaden and finally are not resolved at ~162 K. This observation is consistent with a simple dipolar interaction which increases with increased density of the magnetic states.

The X-ray crystal structure investigation [5] of the furan complex has revealed the dimeric structure shown in Fig. 6 where R = C_4H_3O. The compound crystallizes in a monoclinic space group with either *C2/c* or *Cc* symmetry with four dimeric units per cell. The vanadium pairs are bridged by four carboxylate groups with the fifth coordination site occupied by a cyclopentadiene ring. The vanadium—vanadium separation is 3.63 Å with a mean V—O bond length of 2.04 Å. The mean V—O—C—O—V— bridge length is 6.53 Å [5]. An additional member of this series (R = CF_3) has been characterized [6] by X-ray methods and is structurally similar to the furan complex. In view of the similar magnetic properties of this series, the acetate and benzoate complexes are assumed to be dimeric with the molecular structures indicated in Fig. 6.

The relatively large exchange interactions observed for these complexes are comparable to the interactions found in the structurally similar copper(II) carboxylate systems. For the copper(II) systems, a number R-groups have been used (primarily aliphatic) where the fifth coordination site is occupied by water or an amine. The Cu—O bond lengths are in the 1.92-2.03 Å range and the total bridge length is typically ~6.45 Å [1]. The most obvious structural distinction to be made between the copper and vanadium systems is the different metal—metal separations; the copper—copper separations being in the 2.58-2.75 Å range. Despite the much greater vanadium—vanadium separations, which definitely preclude incipient bond formation, the observed magnetism of both systems is similar. The singlet—triplet energy separations for the copper(II) complexes are in the 250-550 cm^{-1} range while for the present systems this energy difference is in the 235-255 cm^{-1} range (in the absence of biquadratic exchange). This apparent decrease in exchange energy is accompanied by a 0.1 Å increase in total bridge length. Of course, a quantitative comparison of the two systems is impossible since different orbitals are involved in the magnetic interaction.

The comparison of the copper and vanadium systems as well as the evaluation of substituent effects within the vanadium series is hindered by the biquad-

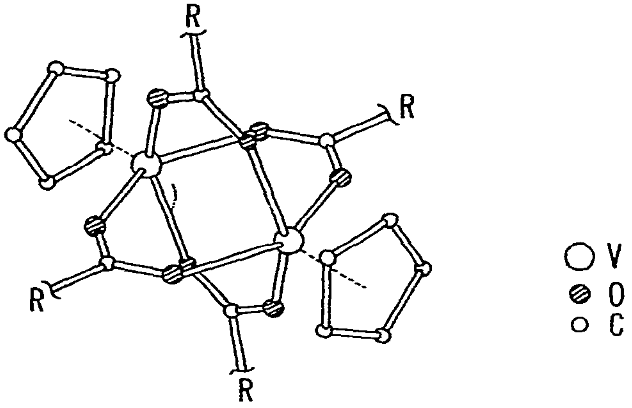

Fig. 6. The molecular structure of the $[CpV(OOCR)_2]_2$ complexes (adapted from ref. 5).

ratic exchange interaction. As seen from Fig. 1 and Table 2, the biquadratic term definitely improves the theoretical fit to the experimental data although seemingly very large biquadratic parameters were required. The values for j derived for the present systems may be compared to biquadratic parameters derived for chromium(III)—chromium(III) pairs. The ratios j/J for the present systems range from 0.075 to 0.197. The corresponding ratios for μ-hydroxybis[pentaminechromium(III)] [15], di-μ-hydroxybis[glycinatochromium(III)] [16], and the Cr^{III}—Cr^{III} pairs doped into $MgAl_2O_4$ [17] are 0.11, 0.10, and 0.075, respectively. For the chromium complexes, however, both exchange parameters are much smaller in magnitude.

Recent theoretical work has shown that the best rationale for the biquadratic term is not intrinsic higher order exchange-only, but that the physical source of biquadratic term is manifested in exchange striction [18]. The exchange striction arises from the dependence of the bilinear exchange on the interspin distance which differs for differing total spin states and a balance between the elastic and exchange forces is achieved. Lines has shown [18] that the effects of exchange striction results in a slight temperature dependence of the bilinear parameter and produces a biquadratic term. The biquadratic parameter is approximated [17,19] as:

$$j \simeq \frac{1}{2}[(\partial J/\partial r)/c]^2 \tag{8}$$

where r is the equilibrium interspin distance and c the elastic stiffness component along the direction of r. As seen from eqn. 8, the biquadratic term is not independent of the bilinear term. This is consistent with the data in Table 2 as well as the increase in j/J of the vanadium systems over the chromium complexes. However, it should be noted that our treatment did not consider the temperature dependence of the bilinear term and, therefore, the actual values for the biquadratic parameters are not necessarily reliable since J and j are highly correlated.

Finally, we note that the magnetic properties observed for vanadium complexes are very similar to the copper acetate analog [20] $Cu_2Ac_4 \cdot pyz$ (pyz = pyrazine) which consists of Cu_2Ac_4 dimeric units bridged by the pyz rings. The

Cu_2Ac_4pyz complex has a singlet—triplet separation of 325 cm^{-1} and an intedimer interaction of ~1100 G. The characteristic 7 line hyperfine interaction, which shows a temperature dependence similar to Fig. 5, was not exchange averaged by the interpair interaction because of significant exchange striction forces [20].

Acknowledgements

This research was supported by the National Science Foundation through grant GP-22887 and by the Materials Research Center of the University of North Carolina through grant GH-33632 from the National Science Foundation. V.T. Kalinnikov thanks the National Academy of Sciences (U.S.A.) for support of his research while an Exchange Scientist Visitor at the University of North Carolina. We wish to thank Professor H.H. Dearman for use of his equipment.

References

1 W.E. Hatfield and R. Whyman, Trans. Metal. Chem., 5 (1969) 47.
2 A.K. Gregson, R.L. Martin and S. Mitia, Proc. Roy. Soc. London Ser. A, 320 (1971) 473.
3 J.N. Van Niekerk and F.R.L. Schoening, Acta Crystallogr., 6 (1953) 227; G.M. Brown and R. Chidambaram, Acta Crystallogr., B, 29 (1973) 2393.
4 V.T. Kalinnikov, V.V. Zelentsov, G.M. Larin, A.A. Pasynskii, and O.D. Ubozhenko, Zh. Obshch. Khim., 42 (1972) 2692.
5 N.I. Kirillova, A.I. Gusev, A.A. Pasynskii and Yu. T. Struchkov, Zh. Strukt. Khim., 13 (1972) 880.
6 G.M. Larin, V.T. Kalinnikov, G.G. Aleksandrov, Yu.T. Struchkov, A.A. Pasynskii and N.E. Kolobova, J. Organometal. Chem., 27 (1971) 53.
7 W.E. Hatfield, C.S. Fountain and R. Whyman, Inorg. Chem., 5 (1966) 1855.
8 B.N. Figgis and R.S. Nyholm, J. Chem. Soc., (1958) 4190; H. St. Räde, J. Phys. Chem., 77 (1973) 424.
9 E. König, Landolt-Börnstein, New Series, Group II, Vol. 2, Springer, Berlin, 1966.
10 A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford University Press, 1970.
11 C. Chao, J. Magn. Reson., 10 (1973) 1.
12 J. Owen, J. Appl. Phys., 32 (1961) 213S.
13 K.T. McGregor, T. Lund and W.E. Hatfield, Spectrosc. Lett., 6 (1973) 309.
14 T. Lund and W.E. Hatfield, J. Chem. Phys., 59 (1973) 885.
15 H. Ikeda, I. Kimura and N. Uryû, J. Chem. Phys., 48 (1968) 4800.
16 J.T. Veal, W.E. Hatfield, D.Y. Jeter, J.C. Hempel and D.J. Hodgson, Inorg. Chem., 12 (1973) 342.
17 J.C.M. Henning and H. van den Boom, Phys. Rev. B, 8 (1973) 2255 and references therein.
18 M.E. Lines, Solid State Commun., 11 (1972) 1615 and references therein.
19 C. Kittel, Phys. Rev., 120 (1960) 335.
20 J.S. Valentine, A.J. Siverstein and Z.G. Soos, J. Amer. Chem. Soc., 96 (1974) 97.