Extending Miedema's model to our ternary alloy systems RE[Os,Ir]$_4$B$_4$, we compare the following posssibilities:

$$\mathrm{Ce^{III}(metal) + 4IrB \rightarrow Ce^{III}Ir_4B_4\ (trivalent)} \quad \Delta H_f^{\mathrm{III}}$$

$$\mathrm{Ce^{IV}(metal) + 4IrB \rightarrow Ce^{IV}Ir_4B_4\ (tetravalent)} \quad \Delta H_f^{\mathrm{IV}}$$

and analogously for the europium-containing compound

$$\mathrm{Eu^{II}(metal) + 4IrB \rightarrow Eu^{II}Ir_4B_4\ (divalent)} \quad \Delta H_f^{\mathrm{II}}$$

$$\mathrm{Eu^{III}(metal) + 4IrB \rightarrow Eu^{III}Ir_4B_4\ (trivalent)} \quad \Delta H_f^{\mathrm{III}}$$

For the difference $\Delta(\Delta H_f)$ for each pair of reactions we calculate in the first case, $\mathrm{Ce^{III} \rightarrow Ce^{IV}}$, 206.7 kJ mol^{-1} and in the second case, $\mathrm{Eu^{II} \rightarrow Eu^{III}}$, 98.7 kJ mol^{-1}. Due to the very similar values for Os and Ir metal according to Miedema's model, it is impossible to differentiate between the heats of formation of, e.g., $\mathrm{CeOs_4B_4}$ and $\mathrm{CeIr_4B_4}$. However, the values $\Delta(\Delta H_f)$ obtained for a valence change in [Ce,Eu][Os,Ir]$_4$B$_4$ alloys are approximately enough to overcome the excitation $\mathrm{Ce^{III} \rightarrow Ce^{IV}}$ metal, in excellent accord with the experimental observations on the pseudobinary system $\mathrm{CeOs_{4-x}Ir_xB_4}$.

Similarly, the thermodynamic values for Eu[Os,Ir]$_4$B$_4$ indicate this system again to be at the borderline for a $\mathrm{Eu^{II} \rightarrow Eu^{III}}$ valence change. This is reflected in the experimental observation of a slightly smaller magnetic moment of the $\mathrm{EuOs_4B_4}$ compound (i.e., small fraction of $\mathrm{Eu^{3+}}$).

Superconductivity. None of the compounds listed in Tables I and II showed any superconducting transition down to a temperature of 1.5 K.

Acknowledgment. This investigation was sponsored by the Air Force Office of Scientific Research under Grant No. 80-0009 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University. P.R. wishes to express his gratitude to DEGUSSA (Deutsche Gold und Silberscheideanstalt), Hanau, Federal Republic of Germany, for supplying noble metals. His thanks are also due to the Austrian Science Foundation (Fonds zur Förderung der wissenschaftlichen Forschung in Österreich) for Grant No. 3620. K.H. thanks the Austrian Science Foundation for the use of the SUS 10 under Grant No. 2950.

Registry No. $\mathrm{EuOs_4B_4}$, 80447-57-0; $\mathrm{EuIr_4B_4}$, 80447-59-1; $\mathrm{CeOs_4B_4}$, 69865-87-8; $\mathrm{CeIr_4B_4}$, 69865-86-7; $\mathrm{SmOs_4B_4}$, 69866-01-9; $\mathrm{SmIr_4B_4}$, 69865-95-8; $\mathrm{PrOs_4B_4}$, 69866-00-8; $\mathrm{PrIr_4B_4}$, 69865-94-7.

---

(21) DeBoer, F. R.; Dijkman, W. H.; Mattens, W. C. M.; Miedema, A. R. *J. Less-Common Met.* **1979**, *64*, 241.

(22) Miedema, A. R. *J. Less-Common Met.* **1976**, *46*, 167.

Contribution from the Istituto di Chimica Generale,
Facoltà di Scienze e di Farmacia, University of Florence, Florence, Italy

Unusual Electronic Spectra of the Pseudotetrahedral Complex [Tris((3,5-dimethyl-1-pyrazolyl)ethyl)amine]cobalt(II) Bis(tetraphenylborate)

LUCIA BANCI, CRISTIANO BENELLI, DANTE GATTESCHI,* and FABRIZIO MANI

Received June 9, 1981

In the complex [tris((3,5-dimethyl-1-pyrazolyl)ethyl)amine]cobalt(II) bis(tetraphenylborate), the metal ion is four-coordinate in a distorted tetrahedral geometry. The electronic spectra show d–d transitions at unusually high energies for tetrahedral complexes. Single-crystal polarized electronic spectra and polycrystalline powder EPR spectra were recorded in order to obtain a full understanding of the electronic structure of the complex. The experimental data were interpreted with the angular overlap model. The unusual electronic spectra have been attributed to a high ligand field strength of the pyrazole residues in the ligand.

Introduction

The characterization of the spectral properties of distorted tetrahedral cobalt(II) complexes is of large interest for the possible implications they may have in clarifying the structure of the active site of metalloproteins and metalloenzymes.[1-3]

Recently one of us reported the synthesis and the X-ray characterization of the structure of a four-coordinate cobalt(II) complex formed with the ligand tris((3,5-dimethyl-1-pyrazolyl)ethyl)amine (MeTPyEA), [Co(MeTPyEA)](BPh$_4$)$_2$.[4] The ligand is tetradentate, N–N$_3$, with three nitrogen atoms belonging to a pyrazole group; the fourth is an amine nitrogen. As such it is an interesting model for heterocyclic bases bonding to metal ions.

The cobalt(II) ion is four-coordinate by the MeTPyEA ligand. The coordination environment is a distorted tetrahedron, with an average $\mathrm{N_{ax}}$–Co–$\mathrm{N_{eq}}$ angle of 100°. The observed tetrahedral geometry is hardly reconciled with the electronic spectra since these show high-frequency bands that are not usually seen in tetrahedral cobalt(II) complexes and resemble more closely those of trigonal-bipyramidal cobalt(II) complexes.[5,6]

In order to obtain more information on the electronic structure of [Co(MeTPyEA)](BPh$_4$)$_2$, we decided to record the single-crystal polarized electronic spectra and the EPR spectra of the complex and wish to report here the results. Spectral data of the complex [Co(NCS)(MeTPyEA)]BPh$_4$ will be also reported for comparison purposes.

Experimental Section

The ligand was prepared starting from $\mathrm{N(CH_2CH_2Cl)_3}$ and potassium 3,5-dimethylpyrazolate with a procedure already described.[7] The [Co(NCS)(MeTPyEA)]BPh$_4$ complex was prepared as follows: warm solutions (20 mL) of the ligand (10^{-3} mol) in absolute ethanol and NaBPh$_4$ (10^{-3} mol) in acetone were added in succession to a warm solution (30 mL) of a stoichiometric amount of cobalt(II) dithiocyanate in absolute ethanol. The resulting solution was concentrated and cooled to room temperature to induce crystallization. Anal. Calcd for $\mathrm{C_{46}H_{53}N_8CoBS}$: C, 67.4; H, 6.51; N, 13.7; Co, 7.18. Found: C, 67.2; H, 6.94; N, 13.9; Co, 7.05.

The [Co(MeTPyEA)](BPh$_4$)$_2$ complex was prepared as above starting from a solution of any cobalt(II) halide. Anal. Calcd for

---

(1) Ulmer, D. D.; Vallee, B. L. *Adv. Chem. Ser.* **1971**, *No. 100*.

(2) Bertini, I.; Luchinat, C.; Scozzafava, A. *Inorg. Chim. Acta* **1980**, *46B1*, 85.

(3) (a) Lindskog, S.; Henderson, L. E.; Kannan, K. K.; Lijas, A.; Nyman, P. O.; Strandberg, B. "The Enzymes"; Academic Press: New York, 1971; Vol. V. (b) Thorslund, A.; Lindskog, S. *Eur. J. Biochem.* **1967**, *3*, 117.

(4) Mani, F.; Mealli, C. *Inorg. Chim. Acta* **1981**, *54*, L77.

(5) Ciampolini, M. *Struct. Bonding, (Berlin)* **1969**, *6*, 52.

(6) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.

(7) Mani, F. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 45.

0020-1669/82/1321-1133$01.25/0 © 1982 American Chemical Society

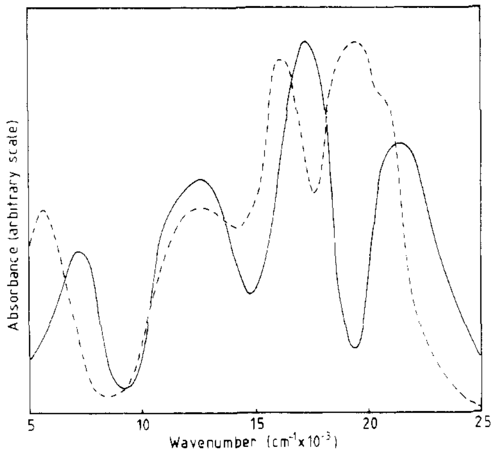

Figure 1. Diffuse-reflectance spectra of (—) [Co(MeTPyEA)](BPh$_4$)$_2$ and (---) [Co(NCS)(MeTPyEA)]BPh$_4$.

$C_{69}H_{73}N_7B_2Co$: C, 76.7; H, 6.81; N, 9.07; Co, 5.45. Found: C, 76.9; H, 7.00; N, 9.34; Co, 5.34. The magnetic susceptibility measurements were performed on a Gouy balance with a procedure described elsewhere.[8]

EPR spectra were recorded at X-band (9-GHz) frequency on a Varian E9 spectrometer, equipped with an Oxford Instruments continuous-flow ESR9 cryostat.

Single-crystal polarized electronic spectra were recorded with a Cary 14 spectrophotometer, using Nicol prisms as polarizers. Single crystals 1.5 × 1.2 × 0.5 mm in size were used. They were gently ground to adjust the absorbance to the spectrophotometer's scale. Low-temperature spectra were recorded with an Oxford Instruments CF 103 cryostat.

Results

The reflectance spectrum of [Co(MeTPyEA)](BPh$_4$)$_2$ is shown in Figure 1. It shows four bands which can be attributed to d–d transitions in the range 7–21 500 cm^{-1}. The absorption spectrum in acetone is substantially similar to the solid reflectance spectrum, and the molar absorption coefficients agree with those usually found for tetrahedral complexes. In Figure 1 is shown also the reflectance spectrum of the complex [Co(NCS)(MeTPyEA)]BPh$_4$, which, from molar conductivity measurements, is expected to be five-coordinate. In the electronic spectra of the solid compound and of the acetone solution, four bands are seen in the range 5–20 000 cm^{-1}, with the band maxima which are in general shifted to lower frequencies as compared to [Co(MeTPyEA)](BPh$_4$)$_2$. Also the molar absorption coefficients decrease, with the exception of the highest frequency band which is almost twice as intense in the thiocyanate derivative.

The magnetic moment of [Co(MeTPyEA)](BPh$_4$)$_2$ is 4.22 μ_B, which corresponds to the lower limit of values observed for pseudotetrahedral cobalt(II) complexes,[9] while the value for [Co(NCS)(MeTPyEA)]BPh$_4$ is 4.43 μ_B, which is in line with the values expected for trigonal-bipyramidal cobalt(II) complexes.[5,6]

The single-crystal polarized electronic spectra were recorded with the incident light perpendicular to the (110) and ($\bar{1}$10) faces and are reported in Figure 2. In the (110) face the crystal appeared dichroic: red when the electric vector was parallel to the *c* direction, which we assume as the laboratory *x* axis, and blue orthogonal to that (the *y* laboratory axis). The highest and the lowest frequency bands are neatly polarized, showing only residual intensity in the perpendicular direction. The other two bands show a reverse polarization pattern, although their polarization ratio is smaller.

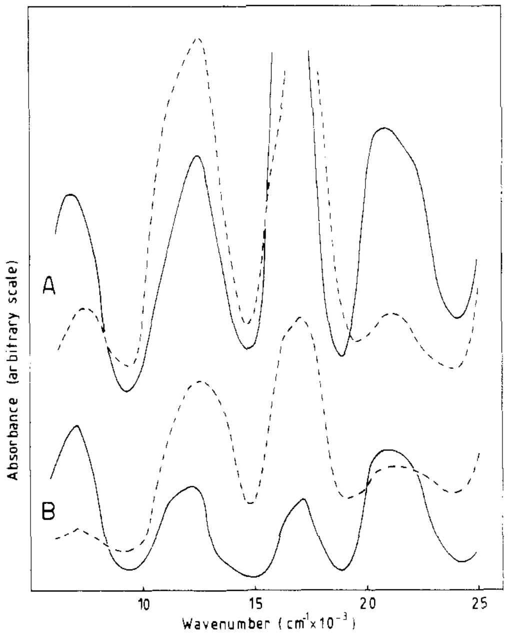

Figure 2. Single-crystal linearly polarized electronic spectra of [Co(MeTPyEA)](BPh$_4$)$_2$. (A) Light perpendicular to the ($\bar{1}$10) face: (—) electric vector parallel to *c*, (---) electric vector orthogonal to *c*. (B) Light perpendicular to the (110) face: (—) electric vector parallel to *c*, (---) electric vector orthogonal to *c*.

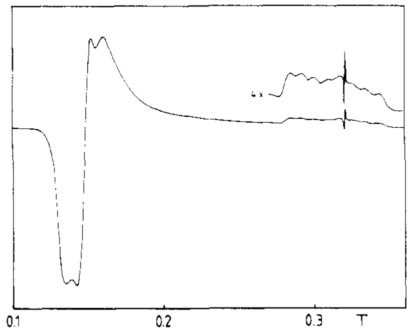

Figure 3. Polycrystalline powder EPR spectrum of [Co(MeTPyEA)](BPh$_4$)$_2$ at X-band frequency and 4.2 K.

The spectra were recorded on the ($\bar{1}$10) face with the electric vector of the incident radiation parallel to the *c* axis and orthogonal to it. Also in this case some polarization was found although not as great as that in the other face. Again the highest and lowest frequency bands show the same polarization while the two intermediate frequency bands are polarized in the reverse sense.

The polycrystalline powder EPR spectrum recorded at 4.2 K is shown in Figure 3. It is a typical spectrum of high-spin cobalt(II) in low-symmetry environments which can be interpreted with an effective spin Hamiltonian with $S = {}^1/_2$ to give $g_1 = 2.05$, $g_2 = 4.0$, $g_3 = 4.7$, and $A_1 = 80 \times 10^{-4}$ cm^{-1}. The signals in the $g = 4$ region have an unusual shape, which may be due to unresolved hyperfine interaction in the magnetically non diluite material.

Attempts were made to record also the single-crystal EPR spectra, but the crystals were found to fracture at the low temperature required by the spectra, irrespective of the slowness in the cooling procedure. We do not know the origin of this behavior although the existence of a phase transition may be suspected. However, electronic absorption spectra on powders at temperature close to 4.2 K do not show any significant variation from the room-temperature spectra, thus showing that the low-temperature EPR spectra can be used to characterize the chromophore.

---

(8) Sacconi, L.; Cini, R.; Ciampolini, M.; Maggio, F. *J. Am. Chem. Soc.* **1960**, *82*, 3487.

(9) Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 2141.

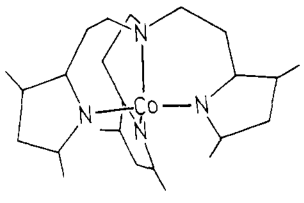

Figure 4. Sketch of the Co(MeTPyEA) cation.

Table I. Squared Components of the Co-N$_{ax}$ Bond Direction in an Orthogonal Reference Frame[a]

	x	*y*	*z*
Co-N$_{ax}$	0.0477	0.2154	0.7369

[a] The *z* axis of the reference frame is coincident with the crystallographic *c* axis.

Discussion

The ground state for a tetrahedral cobalt(II) complex is $^4A_2$. In the present compound, the crystal symmetry of the cobalt(II) ion is C_1, but it is useful to assume a C_{3v} symmetry for the interpretation of the polarization properties. A sketch of the complex is shown in Figure 4. In this group the ground state is $^4A_2$ and the excited levels are either ^4E or $^4A_2$. The polarization pattern therefore was a very simple one, where only $^4A_2 \rightarrow {}^4A_2$ or $^4A_2 \rightarrow {}^4E$ transitions are expected (‖ and ⊥ refer to the C_3 axis). Only one level would be labeled as $^4A_1$, and the transition $^4A_2 \rightarrow {}^4A_1$ is forbidden.

The trigonal axis of the C_{3v} symmetry would be parallel to the Co–N$_{ax}$ direction. Its squared components along the *x*, *y*, *z* laboratory axes which are proportional to the intensity of the polarized transitions are given in Table I. It is apparent that the 7100- and 21 500-cm^{-1} bands are ‖ polarized, so that they can be attributed to $^4A_2 \rightarrow {}^4A_2$ transitions, while the 12 600- and 17 300-cm^{-1} bands are ⊥ polarized and can be attributed therefore to $^4A_2 \rightarrow {}^4E$ transitions. The asymmetric shape of the 12 600-cm^{-1} band can be due to low-symmetry components of the ligand field which destroy the axial symmetry assumed for the assignment. The molar absorption coefficients in solution of the four bands agree with those expected for d–d transitions.

The EPR spectra are in agreement with a $^4A_2$ ground level largely split in the zero field as shown by a $g_\parallel$ value close to 2 and $g_\perp$ close to 4. The symmetry of the complex is not very far from axial as shown by the moderate splitting of $g_\perp$. In fact the present values can be compared with those of [CoBr$_3$(quinoline)]$^-$, which yields $g_1 = 1.61$, $g_2 = 2.33$, and $g_3 = 6.51$[9], and those of [Co(Ph$_3$PO)$_2$Cl$_2$], which yields $g_1 = 2.16$, $g_2 = 3.59$, and $g_3 = 5.7$.[10] Using an approximate analysis which sets $g_x = g_y = g_\perp$, it is possible to calculate the true *g* values of the $S = {}^3/_2$ ground state and the E/D ratio, λ,[11] which is a measure of the rhombicity of the coordination environment. For $\lambda = 0$, the symmetry is axial, while for $\lambda = {}^1/_3$, the rhombicity is maximum. For [CoBr$_3$ (quinoline)]$^-$, we calculate $g_\parallel = 2.15$, $g_\perp = 2.48$, and $\lambda = 0.321$, for [Co(Ph$_3$PO)$_2$Cl$_2$], $g_\parallel = 2.31$, $g_\perp = 2.35$, and $\lambda = 0.152$, and for the present complex, $g_\parallel = 2.05$, $g_\perp = 2.18$, and $\lambda = 0.054$. Although the above treatment is surely an approximate one, it is expected to yield a reasonable measure of the rhombicity of the spectra.

The striking feature of the electronic spectra of the [Co(MeTPyEA)](BPh$_4$)$_2$ derivative is the high energy of some of the transitions, at least if one compares them to those of typical tetrahedral complexes. For instance, for the [Co(H$_2$B(pz)$_2$)$_2$] complex (H$_2$B(pz)$_2$ is dihydrobis(1-pyrazolyl)borate) in which four pyrazole donors are present, the lowest A$_2$ and E transitions are a 8200 and 9300 cm^{-1}, while the ^4F–^4P transitions range from 17 000 to 19 000 cm^{-1}.[12]

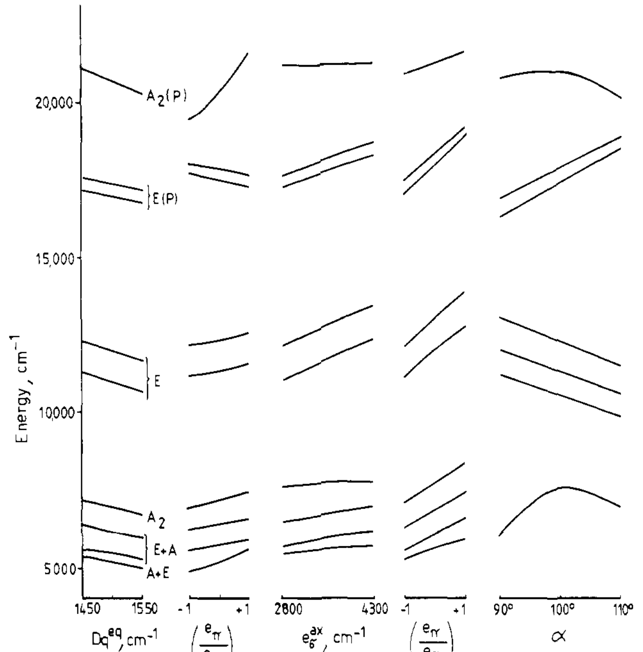

Figure 5. Energy level diagram for [Co(MeTPyEA)](BPh$_4$)$_2$. Left: the effect of varying $Dq^{eq} = (3e_\sigma^{eq} - 4e_\pi^{eq})$, with $e_\sigma^{ax} = 3800$ cm^{-1}, $e_\pi^{ax} = 0$ cm^{-1}, $(e_\pi/e_\sigma)^{eq} = 0.1$, $B = 750$ cm^{-1}, $\zeta = 533$ cm^{-1}, and $\kappa = 0.8$. From left to right is shown the effect of varying the parameters at the bottom in turn, leaving all the others unchanged, with $Dq^{eq} = 1510$ cm^{-1}. In the case of variation of the angle N$_{ax}$–Co–N$_{eq}$, α, the $(e_\pi/e_\sigma)^{eq}$ is 0.07.

A somewhat more similar pattern of bands is observed for some trigonal-bipyramidal complexes containing CoN$_4$Br chromophores[13] such as [CoBr(Me$_6$tren)]$^+$ (Me$_6$tren is tris(2-(dimethylamino)ethyl)amine), which shows transitions at 5700, 12 300, 16 100, and 19 500 cm^{-1}, and [Co(NCS)(Me$_6$tren)]$^+$,[14] which shows transitions at 5800, 14 800, 16 500, and 21 000 cm^{-1}. On the other hand, the lowest frequency band (at 7100 cm^{-1}) of the present cobalt(II) complex is compatible with a tetrahedral geometry but too high for trigonal-bipyramidal coordination. It must also be mentioned that compared to the trigonal-bipyramidal complexes referenced above,[14] the polarization pattern of the highest and lowest frequency bands is reversed in the present case.

In order to confirm these observations we used the angular overlap model[15] to calculate the electronic energies and the spin Hamiltonian parameters of the complex. In the calculations we assumed $e_\pi = 0$ for the axial nitrogen donor atom and isotropic interactions for the equatorial donors. In figure 5 we show some calculated energy level patterns as a function of the AO parameters. The geometrical coordinates we used are those seen in the X-ray crystal structure determination.[4] Although the symmetry of the levels is lower than axial, actually C_1, we used the preponderant classification in C_{3v} symmetry.

From Figure 5 it is apparent that provided that the e_σ value for the axial nitrogen donor is kept smaller than that of the equatorial ones, the pattern of the energy levels corresponds

---

(10) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C.; *Inorg. Chem.* **1979**, *18*, 2137.

(11) Desideri, A.; Morpurgo, L.; Raynor, J. B.; Rotilio, G. *Biophys. Chem.* **1978**, *8*, 267.

(12) (a) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *8*, 267. (b) Guggenberger, L. J.; Prewitt, C. T.; Meakin, P.; Trofimenko, S.; Jesson J. P. *Inorg. Chem.* **1973**, *12*, 508.

(13) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41.

(14) Bertini, I.; Ciampolini, M.; Gatteschi, D. *Inorg. Chem.* **1973**, *12*, 693.

(15) Schaffer, C. E. *Struct. Bonding (Berlin)* **1968**, *5*, 68.

Table II. Best Fit of Energy Transitions and g and μ_{eff} Values

Energy of Transition, cm^{-1}

calcd	obsd	calcd	obsd
5303		17 739	17 300
5417		17 797	
5658		18 161	
5736		18 232	
6425		21 405	
6471		21 417	21 400
7212	7100		
7366			
11 354			
11 504			
12 411			
12 506	12600		

g Values

	calcd	obsd		calcd	obsd
g_1	2.04	2.05	g_3	4.84	4.7
g_2	3.86	4.0			

μ_{eff} Values, μ_B

temp, K	obsd	calcd	temp, K	obsd	calcd
300	4.22	4.22	88	4.24	4.18

to the observed ones, with a sequence of excited levels in order of decreasing energy: A_2, E, E, A_2. Actually the order of the levels in the low-frequency region is not so well settled since many overlapping levels are present.

The usual variation of the e_π/e_σ ratio, although affecting to some extent the energy of the levels, does not greatly modify their order. It affects however to some extent the relative energies of the highest $^4A_2$ and ^4E levels, negative values tending to decrease the separation.

We wanted also to check what might be the effect on the energy levels of varying the N_{ax}–Co–N_{eq} angle in the range from 109.44°, the tetrahedral value, to 90°. The computed levels are shown in Figure 5. It is apparent that with this variation the $^4A_2(P)$–$^4E(P)$ separation tends to increase, as does also the energy of ^4E relative to the ground $^4A_2$ level. The levels in the low-frequency region follow a less definite pathway. In particular the energy relative to the ground state of the lowest $^4A_2$ levels is calculated to have a maximum at ~100°.

The best fit of the electronic transitions we were able to find is given in Table II together with the calculated g and μ values. The agreement is fully satisfactory for all the calculated properties. The values of the parameters used for the equatorial donors are much larger than usually found for pyrazole-type ligands.[16-21] As a matter of fact, the calculated Dq value ($Dq = 3e_\sigma - 4e_\pi$) for the equatorial ligand is 1500 cm^{-1}, much higher than 1000 cm^{-1} suggested by Jesson for poly(pyrazolyl)borates[12a] and also much higher than the value of 1100 cm^{-1} found by Reedijk[20] and 1200 cm^{-1} found by us for pyrazole.[17]

If we try to understand the large Dq value required for the equatorial donor atoms, a structural comparison may be required. As a matter of fact in the present case the metal to equatorial nitrogen distance is on the average 194 pm,[4] which is somewhat shorter than the average 197 pm seen in the poly(pyrazolyl)borate complexes[12b] and much shorter than the 200–215 pm seen in the octahedral pyrazole complexes.[22] Although it may be surprising that a variation of 3 pm determines such a large increase in the ligand field strength, we believe that this is the only rationale for justifying the unusal electronic spectra of $[Co(MeTPyEA)](BPh_4)_2$.

Registry No. $[Co(MeTPyEA)](BPh_4)_2$, 77417-18-6; $[Co(NCS)(MeTPyEA)]BPh_4$, 77417-20-0.

---

(16) Reedijk, J.; Harsen, J. C.; van Koningsveld, H.; van Kralingen, C. G. *Inorg. Chem.* **1978**, *17*, 1990.

(17) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1980**, *19*, 1301.

(18) Roundhill, S. G. N.; Roundhill, D. M.; Bloomquist, D. R.; Landee, C.; Willett, R. D.; Dooley, D. M. Gray, H. B. *Inorg. Chem.* **1979**, *18*, 831.

(19) O'Young, C. L.; Devon, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291.

(20) Vermaas A.; Groenevald, W. L.; Reedijk, J. *Z. Naturforsch., A* **1977**, *32A*, 632.

(21) Thompson, J. S.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4193.

(22) Reimann, C. W.; Mighell, A. D.; Maner, A. F. *Acta Crystallogr.* **1967**, *23*, 135.

Contribution from the Departments of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390, Japan,
and Miami University, Oxford, Ohio 45056

^{19}F and ^{13}C NMR Study of the Kinetics of Ligand-Exchange Reactions in Oxovanadium(IV) Complexes

OSAMU YOKOYAMA, HIROSHI TOMIYASU, and GILBERT GORDON*

Received January 6, 1981

The kinetics of fluoride ion exchange in the oxovanadium(IV) glycine and fluoride mixed complex, $VO(gly)glyF^-$, and oxalate exchange in (dioxalato)oxovanadium(IV), $VO(ox)_2^{2-}$, have been studied by means of ^{19}F NMR and ^{13}C NMR methods. The equilibrium and formation reactions of these complexes have also been studied by using spectrophotometric and stopped-flow measurements. In every case, the reactions were found to be first order in both the entering ligand and the VO^{2+} complex. The overall rate is determined primarily by the charge on the ligand and on the complex, and the chelation process is not dissociation controlled. The activation parameters obtained are as follows: for F^- exchange on $VO(gly)glyF^-$, $\Delta H^* = 33._2 \pm 1._6$ kJ mol^{-1} and $\Delta S^* = -51._7 \pm 5._3$ J K^{-1} mol^{-1}; for oxalate exchange on $VO(ox)_2^{2-}$, $\Delta H^* = 39._8 \pm 1._9$ kJ mol^{-1} and $\Delta S^* = -51._6 \pm 5._8$ J K^{-1} mol^{-1} at pH 6.50 and $\Delta H^* = 51._0 \pm 2._6$ kJ mol^{-1} and $\Delta S^* = -7._6 \pm 8$ J K^{-1} mol^{-1} at pH 2.89.

During the past decade the kinetics of ligand substitution reactions for oxovanadium(IV) complexes have been of particular interest.[1-12] The ^{17}O NMR studies[1-3] were important in the early studies, which were concerned with the water-exchange reaction for $VO(H_2O)_5^{2+}$ and other related com-

---

* To whom correspondence should be addressed at Miami University.

(1) Reuben, J.; Fiat, D. *Inorg. Chem.* **1967**, *6*, 579.

(2) Wuthrich, K.; Connick, R. E. *Inorg. Chem.* **1967**, *6*, 583.

(3) Wuthrich, K.; Connick, R. E. *Inorg. Chem.* **1968**, *7*, 1377.

(4) Tomiyasu, H.; Dryer, K.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 2409.

(5) Tomiyasu, H.; Ito, S.; Tagami, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2843.

(6) Tomiyasu, H.; Gordon, G. *Inorg. Chem.* **1976**, *15*, 870.

(7) Nishizawa, M.; Saito, K. *Inorg. Chem.* **1978**, *17*, 3676.

(8) Nishizawa, M.; Saito, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 483.

(9) Angerman, N. S.; Jordan, R. E. *Inorg. Chem.* **1969**, *8*, 65.

0020-1669/82/1321-1136$01.25/0