is a paramagnet with $S = {}^1/_2$, and the g value is reduced to 1.79. Also, a complex hyperfine spectrum is observed. The low g value indicates appreciable spin transfer between the iridium and the chlorine atoms. The hyperfine field has been adequately explained in terms of a coupling interaction of iridium electron spin and chlorine nuclear spin. It has been shown that the t_{2g} orbital hole responsible for the ESR is delocalized over the chlorine ligands to the extent that $\sim$70% resides on the central iridium cation. The preceding spin delocalization effects are observed in terms of the *single-ion* ($\mathrm{Ir^{4+}}$) ESR spectrum. In the present work, we are extending their observation to *ordering of delocalized spin density for the* $\mathit{FeCl_6^{3-}}$ *clusters* where nonbonded Cl–Cl contacts are probably at the van der Waals radius. While the single-crystal structure of $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$ has not been determined, those of the related complexes $[\mathrm{Co(NH_3)}][\mathrm{MCl_6}]$, M = Tl, Sb, have been. A partial packing structure[15] of $[\mathrm{Co(NH_3)_6}][\mathrm{SbCl_6}]$ is shown in Figure 8. The complex packs in an NaCl structure containing four anions and four cations per unit cell. The $\mathrm{SbCl_6^{3-}}$ chromophore is in an essentially octahedral environment, with the interanionic Cl–Cl contact distance of 3.79 Å. In addition, *hydrogen bonding* between the cation and anion is clearly indicated by the shorter N–Cl distances, between 3.2 and 3.4 Å. This hydrogen bonding introduces the possibility of complex cation involvement in the magnetic interactions. We hope to study this aspect for $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$ in the near future by cobalt-57 emission Mössbauer spectroscopy studies. If the cation participates in the magnetic interaction, there may well be a transfer of magnetic hyperfine field to the normally diamagnetic cobalt (low-spin d^6 Co(III)) and this can be observed in such emission spectra.

To conclude, we note that our iron-57 Mössbauer spectroscopy study of $[\mathrm{Co(NH_3)_6}][\mathrm{FeCl_6}]$ shows no evidence of magnetic ordering to 1.6 K. The crystal structure of this material has recently been determined.[16] Using the published unit cell parameters and the appropriate atomic coordinates, we have searched for inter $\mathrm{FeCl_6^{3-}}$ anion Cl–Cl contacts less than 4.2 Å and find none. Subsequently, one of the investigators of ref 16 (J. Beattie) furnished us with the results of a similar search of the data with the same result, i.e., no Cl–Cl contacts <4.2 Å. For the present, we *speculate* that the apparent much weaker zero exchange in $[\mathrm{Co(NH_3)_6}][\mathrm{FeCl_6}]$ is the result of somewhat larger contact distances and/or weaker hydrogen bonding. A simple varient of $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$, namely $[\mathrm{Co(en)_3}][\mathrm{FeCl_6}]$ (en = ethylenediamine), is also currently under investigation.

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Registry No. $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$, 20519-29-3.

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Vibrational Fine Structure of the $^1B_g \leftarrow {}^1A_g(C_{2h})$ Absorption Band of *trans*-$[\mathrm{Co(CN)_2(en)_2}]^+$. Excited-State Conformation

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The 4.2 K polarized absorption, polarized infrared, and Raman spectra of *trans*-$[\mathrm{Co(CN)_2(en)_2}]\mathrm{ClO_4}$ and its deuterated analogue have been measured. The vibronic spectra due to the first spin-allowed transition, $^1B_g \leftarrow {}^1A_g$, of small single crystals exhibit distinct vibrational structure from a progression created by a single accepting mode of 236-cm^{-1} frequency. A normal-coordinate analysis identified this mode as being derived from almost equal contributions of Co–N and N–C stretching and NCoN angular vibrations, with a fundamental frequency of 269 cm^{-1} in the ground state. A least-squares fit of the theoretical band profile function to the experimental spectra determined the spectroscopic parameters, which allowed an estimation of the equilibrium geometry changes due to electron excitation.

Introduction

In a previous paper[1] the change in equilibrium geometry of *trans*-$[\mathrm{Co(CN)_2(NH_3)_4}]^+$ in the ligand field excited state, $^1A_{2g}(D_{4h})$, relative to the ground state, $^1A_{1g}$, was determined from the intensity distribution in the vibrational progression of the polarized absorption spectrum. The present study extends this investigation to single crystals of the corresponding chelate complex *trans*-$[\mathrm{Co(CN)_2(en)_2}]^+$, which requires a more elaborate theoretical analysis because of the presence of ring systems.

In general, ligand field spin-allowed absorption spectra of transition-metal complexes can be resolved into vibrational components only on rare occasions; e.g., vibrational structure has been reported for the first spin-allowed transitions in the absorption and the circular dichroism spectra of cobalt(III) complexes with ethylenediamine, tetramethylenediamine, and octaazabicycloeicosane ligands.[2,3]

The spectra of these compounds, however, did not permit resolution of vibronic (false) origins, because of the overlapping of the large number of band components. A relatively simple chelate-containing system, which exhibits sufficiently well-resolved absorption spectra, was found in *trans*-$[\mathrm{Co(CN)_2}$-

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$(en)_2]ClO_4$ and its N-deuterated analogue. The polarized single-crystal spectra of the $^1B_g \leftarrow {}^1A_g$ band from these two complexes exhibited a series of false origins (Herzberg–Teller vibronic mechanism) and a single progression built up on each of these origins. The spectroscopic results are presented below, together with an analysis of the intensity pattern. Following a procedure outlined in the earlier paper,[1] an estimate of the excited-state geometry was obtained by using a normal-coordinate calculation performed for the electronic ground state.

Experimental Section

Preparation of Compounds. The complex *trans*-$[Co(CN)_2(en)_2]Cl$ was prepared according to a method described previously.[4] The compound was converted to the perchlorate by adding $NaClO_4{\cdot}6H_2O$ to an aqueous solution of the chloride. Anal. Calcd: Co, 17.83. Found: Co, 17.77. The complex was deuterated by repeated evaporation of a D_2O solution of the perchlorate. Anal. Calcd: Co, 17.40. Found: 17.39. Infrared absorption spectra indicated satisfactory deuterium substitution in the compound. Thin single crystals, suitable for electronic and infrared transmission spectroscopy, were grown over a period of 1 week from an aqueous solution of the complex perchlorate and of $NaClO_4{\cdot}6H_2O$, which were mixed very slowly from different branches of a U-tube. For the deuterated compound, a D_2O solution of the deuterated complex perchlorate and sodium perchlorate that had been twice recrystallized from D_2O were used. Larger single crystals, used for transmission spectroscopy in the band-origin region, were grown from a slowly evaporating saturated solution at 23 °C.

Electronic Absorption, Infrared Absorption, and Raman Spectra. Single-crystal polarized absorption spectra at low temperatures were measured as described previously.[1] The equipment was modified by using a liquid-helium flow cryostat, Air Products LT-3-110 C, by which the temperature dependence of the absorption spectra could be measured between 300 and 4.2 K. The thickness of the samples was estimated with a graduated ocular under a microscope.

Infrared absorption spectra were measured on a Perkin-Elmer 325 spectrometer (4000–400 cm^{-1}) and a Beckman IR 720 interferometer (500–20 cm^{-1}). A thin crystal (ca. 1.5 × 1.8 × 0.014 mm) was mounted on a pinhole (o.d. = 1.4 mm) in a small indium plate that was placed into the sample beam. A neutral-density filter was used to attenuate the reference beam. Raman spectra were recorded with a GCA McPherson 0.5-m double monochromator (Model 285) and a light detection system consisting of a cooled RCA C31034 photomultiplier and a Keithley Instruments model 417 picoammeter. The samples were irradiated with the 514.7-nm line of a Spectra Physics Model 165 argon ion laser.

Results and Analysis

Electronic Absorption Spectra. The polarized absorption spectrum of *trans*-$[Co(CN)_2(en)_2]ClO_4$ at 4.2 K is shown in Figure 1. According to an X-ray structure determination performed at room temperature,[5] the crystal is monoclinic, belonging to the space group $C2/c$ ($C_{2h}{}^6$). The parameters for the unit cell are $a = 17.556$ (3) Å, $b = 6.930$ (1) Å, $c = 10.604$ (2) Å, and $\beta = 93.18°$. The unit cell contains four formula units ($Z = 4$), which occupy equivalent positions. The site symmetry of Co is C_i. The X-ray structure results[5] indicate, however, approximate C_{2h} symmetry for the complex molecule; therefore, the analysis is carried out by using this point group of symmetry. The crystals formed plates with an area of ca. 1 mm^2, with faces parallel to the (100) crystal plane. Therefore, the absorption spectra could be measured with incident radiation polarized parallel to the *b* and *c* crystal axes (b and c spectra).

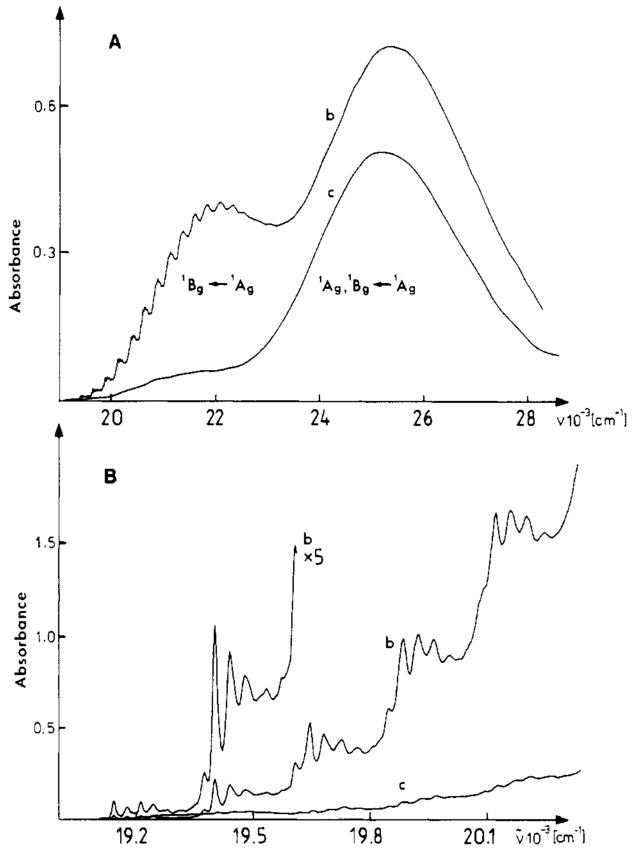

Figure 1. Overall 4.2 K absorption spectra due to the low-energy spin-allowed ligand field transitions of *trans*-$[Co(CN)_2(en)_2]ClO_4$ polarized parallel to the *b* and *c* axes of the unit cell, recorded with crystalline plates of thickness 0.034 mm (A) and (for the long-wavelength region) 0.05 mm (B).

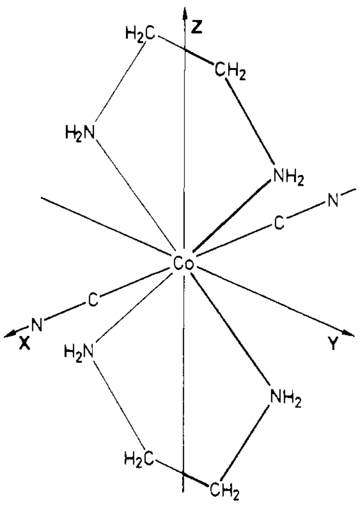

Figure 2. Structure of the *trans*-$[Co(CN)_2(en)_2]^+$ complex (symmetry C_{2h}) with nonplanar ring conformations.

The absorption spectrum was basically similar to that of *trans*-$[Co(CN)_2(NH_3)_4]^+$. The unresolved band with a maximum at 25 300 cm^{-1} corresponds to the transitions ^1A_g, $^1B_g \leftarrow {}^1A_g$, and the band with the pronounced vibrational structure in the low-energy region is assigned to the ^1B_g excited state. The dichroism observed for the $^1B_g \leftarrow {}^1A_g$ band can be interpreted in terms of vibronic selection rules[1] according to which a_u vibrations induce electric dipole transitions polarized parallel to the *x* and *y* directions and a b_u vibration promotes transitions in *z* direction.

Figure 3 shows the single-crystal polarized infrared absorption spectra of the perchlorate crystal (thickness 0.013 mm). The sharp absorption line due to $\nu(C{\equiv}N)$ at 2134 cm^{-1} was found to be polarized mainly along the crystal *c* axis, indicating that the molecular *x* axis of each molecule (which contains the CN ligands, see Figure 2) is approximately

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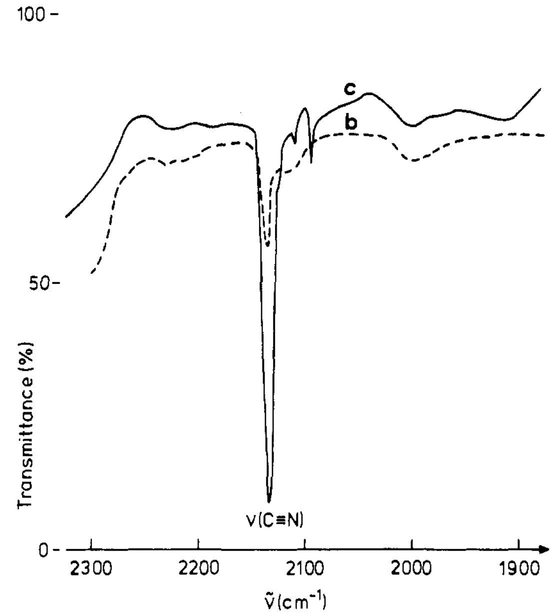

Figure 3. Polarized infrared spectra of *trans*-$[Co(CN)_2(en)_2]ClO_4$ in the C≡N stretching region (polarization; cf. Figure 1).

parallel to the *c* axis. This agrees with the X-ray structure results according to which all molecular *x* axes form a 9° angle with the *c* axis and are inclined out of the *ac* plane by +4°.[5] Thus, the b spectrum in Figure 1 (incident radiation polarized parallel to the *b* crystal axis) is mainly polarized in the *yz* plane, which contains the ethylenediamine rings and is induced by a_u and b_u vibrations. The c spectrum polarized mainly in *x* direction is promoted by a_u vibrations.

A first inspection of the vibronic structure of the $^1B_g \leftarrow {}^1A_g$ band indicates that the spectra at the absorption edge of both compounds investigated are superpositions of two identical groups of vibronic origins (i.e., transitions of the type $\omega_{0-0} + \omega_u$), separated by about 38 cm^{-1}. The weak absorptions at 19140 and 19178 cm^{-1} are assigned to zero phonon transitions. The corresponding vibronic origins in the two groups of vibronic lines have comparable intensities. Since these bands originate from a transition between two nondegenerate states, the presence of two almost identical spectra superimposed on each other must be due to the presence of two nonequivalent complex molecules that are formed at lower temperature by converting the $C_i(4)$ site into two sites of lower multiplicity or by duplication of the unit cell.

Besides the zero phonon lines and about 20 vibronic origins (10 in each of the two series), which we have designated the fundamental spectral pattern,[1] the absorption spectrum contains a long progression with 236-cm^{-1} energy intervals. A least-squares fit of equally spaced Lorentzian curves superimposed on the fundamental spectral pattern yields an excellent agreement with the experimental spectrum, indicating that only one progressional mode is present. The same result is obtained for the N-deuterated complex *trans*-$[Co(CN)_2(en\text{-}d_4)_2]ClO_4$, which has progressional intervals of 220 cm^{-1}. The ground-state vibrational frequencies corresponding to these normal modes are found in the Raman spectra at 269 and 267 cm^{-1}, respectively. These vibrations are assigned to a totally symmetric deformation mode of the chelate ring of the complex (see below). Kanamori et al.[7] have also pointed out that the characteristic Raman lines of *trans*-$[CoXY(en)_2]^+$ (X, Y = halogen, CN) that occur at ca. 270 cm^{-1} can be assigned to the chelate ring mode δ_c. The frequency reduction by about 15% in the electronic excited state relative to the ground state has been detected for other transitions of the type $t_{2g} \rightarrow e_g$ (in O_h).[1,8] The actual geometric distortion in the excited state, corresponding to movement along this particular normal coordinate, is calculated further below.

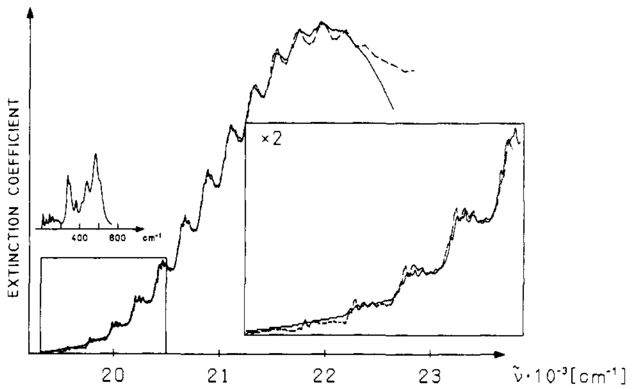

Figure 4. The *b*-polarized experimental (dashed line) and calculated (solid line) $^1B_g \leftarrow {}^1A_g$ absorption spectra of *trans*-$[Co(CN)_2(en)_2]ClO_4$ corrected for the band overlap due to the higher singlet transitions. The fundamental spectral pattern is shown above the low-energy part of the spectrum.

Table I. Force Constants for the $[Co(CN)_2(en)_2]^+$ Cation Resulting from Normal-Coordinate Analysis

force type	atoms involved	k^a	force type	atoms involved	k^a
str	Co-N	1.593	bend	N-C-C	0.989
	N-C	3.385		Co-C-N	0.372
	C-C	2.802	str-bend	Co-N, N-Co-C	0.240
	Co-CN	2.650		Co-N, N-Co-N	0.110
	C≡N	16.90		Co-N, Co-N-C	0.093
str-str	Co-N, Co-N	0.054		N-C, Co-N-C	0.086
	Co-N, N-C	0.059		N-C, N-C-C	0.257
	Co-N, Co-CN	0.081		C-C, N-C-C	0.259
	N-C, C-C	0.117		Co-C, N-Co-C	0.235
	Co-C, C≡N	0.400	torsion	Co-N	0.030
bend	N-Co-C	1.264		N-C	0.100
	N-Co-N	1.531		C-C	0.107
	Co-N-C	0.383			

[a] Force constants in units of mdyn·Å^{-1} (stretch, stretch–stretch), mdyn·Å·rad^{-2} (bend, torsion), and mdyn·rad^{-1} (stretch–bend).

Intensity Distribution. As has been outlined previously,[1] the vibronic spectrum of Figure 1 can be expressed in terms of a line-shape function

$$W(\nu) = \sum_{n=0}^{\infty} f(\nu - n\omega_\delta^{(e)})\ I_1(n;\Delta_\delta,\beta_\delta) \qquad (1)$$

The sidebands at lower energy (fundamental spectral pattern), which contain the pure electronic origins ω_{0-0} and all vibronic origins, are given by eq 1, setting $n = 0$. The line-shape function over the interval from ω_{0-0} to $\omega_{0-0} + 230$ cm^{-1}, i.e. $f(\omega_{0-0} + 230\ \text{cm}^{-1})$, was taken directly from the experimental spectrum (Figure 1B). The intensities, bandwidths, and band maxima of those vibronic origins that have energy quanta higher than that of the accepting mode, giving rise to bands overlapping with the first members of the progression, were estimated from Figure 1B and later used as adjustable parameters in the least-squares fit. The band profile of the progression in the single accepting mode (δ_c) was generated by the intramolecular distribution $I_1(n;\Delta,\beta)$,[9] which depends on parameters containing information about the geometry change, Δ, and vibrational frequency change, β, during the electronic excitation. The quantum number *n* refers to the

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individual members of the single progression. The line-shape function, eq 1, was then compared with the experimental spectrum by varying the band parameters of the vibronic origins (with energies higher than 230 cm^{-1}) and the parameters $\omega_\delta^{(e)}$, Δ, and β (in the intramolecular distribution) as well, until agreement within a given error limit was achieved (see Figure 4). The low-energy flank of the ^1A_g, $^1B_g \leftarrow {}^1A_g$ band was taken into account by deducting a Gaussian-type distribution from the first band. A close fit to the experimental spectrum of *trans*-$[Co(CN)_2(en)_2]^+$ was achieved when the parameter set $\Delta_\delta = 4.8$, $\beta_\delta = 1.15$, and $\omega_\delta^{(e)} = 236$ cm^{-1} was chosen. From the thus determined excited-state vibrational frequency, $\omega_\delta^{(e)}$, and the measured ground-state vibrational frequency, $\omega_\delta^{(g)} = 269$ cm^{-1}, for the H-compound, the quotient $\beta_\delta = \omega_\delta^{(g)}/\omega_\delta^{(e)} = 1.14$ was calculated, which agrees very well with the value obtained from the fitting process. Similar values of the parameters Δ and β were obtained for the deuterated compound. The β parameter reflects the contribution of the antibonding d electrons to the force constants that change the vibrational frequency $\omega^{(e)}$ in the electronically excited state relative to that in the ground electronic state. The value of β determines the skew of the absorption spectral shape, and the parameter Δ the length of the progression.

From the Δ values obtained the displacement in the normal mode ΔQ can be calculated from

$$\Delta Q = (M\omega/\hbar)^{-1/2}\Delta \qquad (2)$$

where M denotes the reduced mass appropriate to the corresponding accepting mode, as obtained from a normal-coordinate analysis (see next section). Moreover, from the transformation matrix between symmetry and normal coordinates, the nuclear displacements in the δ_c mode and, hence, the conformational geometry change in the electronic excited state relative to the ground state can also be calculated.

Normal-Coordinate Analysis and Estimation of the ^1B_g Excited-State Geometry. In principle, all possible totally symmetric normal coordinates of vibration may couple vibronically to both ^1A_g and ^1B_g electronic states and must be considered responsible for the distortion in the geometry of the molecule when excited. In order to determine bond length changes, we make use of the relation

$$Q_i = \sum_j (\mathbf{L}^{-1})_{ij} S_j \qquad (3)$$

that connects the normal coordinate Q_i and the symmetry coordinate S_j by the matrix $\mathbf{L}^{-1}$, which is obtained from a normal-coordinate analysis. Similarly, the force F_i (acting along Q_i) affecting the geometry of the excited molecule is given by

$$F_i = \sum_j \mathbf{L}_{ji} F_{S_j} \qquad (4)$$

where F_{S_j} denotes the distorting force belonging to the *j*th total symmetric coordinate.[1] Since the low-lying absorptions are due to d–d transitions localized on the cobalt ion, contributions F_{S_j} belonging to motions within the chelate rings can be neglected. In addition, for the transition $^1B_g \leftarrow {}^1A_g$ (which corresponds predominantly to an orbital transition $d_{yz} \leftarrow d_{y^2-z^2}$ in the notation of Figure 2), the force associated with the Co–C stretching symmetry coordinate, S_4, vanishes because of the axial symmetry of the dynamical ligand field[1] (or is relatively small, if other d-orbital transitions with the same symmetry intermix). Therefore, the forces can be written, to a good approximation, $F_i = \mathbf{L}_{1i} F_{S_1}$, where S_1 is the symmetric Co–N bond-stretching coordinate.

The normal-coordinate analysis was performed by considering the CH_2 and NH_2 groups in the ring each as single atomic units. The potential function and force constants were assumed to be of the UBFF type,[10] not taking into account the coupling to lattice vibrations (i.e., the intermolecular interactions were assumed to vanish). These have negligible effects on the molecular force constants, since the calculated intramolecular frequencies lie in the region above 200 cm^{-1}. The numerical calculation was carried out by using a OCPE program.[11] Molecular parameters and symmetry coordinates of the chelate rings were taken from Borch et al.[12] Initial values for the force constants were chosen with reference to results obtained for other Co complexes;[10] the resulting constants calculated from the normal-coordinate analysis are given in Table I. The NCoN angles were set equal to 90° instead of the 85.8° determined from the X-ray structure investigation.[5] The result of the fit to vibrational frequencies is given in Table II, in which all totally symmetric modes are listed, as well as those other vibrations for which experimental data are available. Frequencies in the region of 550–650 cm^{-1} belonging to deformation modes have not been included in the table, since these modes couple to the low-energy vibrations of the H–N–H and H–C–H groups at frequencies near 800 cm^{-1},[13] neither of which were included in the model used. The predominant Co–N stretching modes have frequencies around 500 cm^{-1}. The normal-coordinate analysis reveals that the δ_c mode, which is responsible for the distortion when the molecule is eleconically excited, has equally large contributions from Co–N (S_1) and N–C (S_2) stretching motions and from NCoN (S_9) and (S_{10}) angular motions:

$$\Delta Q_{24} \approx 0.44\Delta S_1 - 0.47\Delta S_2 - 0.56\Delta S_9 + 0.47\Delta S_{10} \qquad (5)$$

Contributions from torsional deformations around the Co–N, N–C, and C–C axes are quite small. This indicates that the stretching of the metal–nitrogen bonds changes primarily the NCoN angles (S_9) and (S_{10}), rather than the torsional angles. The corresponding intramolecular force when $^1B_g \leftarrow {}^1A_g$ excitation occurs is $F_{24} = 0.44F_{S_1}$. According to the normal-coordinate analysis, Q_{24} aside, the totally symmetric modes Q_{12}, Q_{14}, and Q_{19} also involve substantial amounts of Co–N stretching, which could also give rise to vibrational progressions in the spectrum. However, these normal modes due to the larger vibrational quanta have steeper energy potentials leading to greater resistances against distortions. Hence, it is reasonable to assume that $\Delta Q_i \approx 0$ (i = 12, 14, 19).

With the reduced mass $M_{\delta(24)} = 37.04$ amu as obtained from the normal-coordinate analysis, the coordinate displacement ΔQ_{24} was calculated from eq 2. Since only the coordinate Q_{24} is active in producing a vibrational progression in the spectrum, from $F_{24} = 0.44F_{S_1}$ we obtain $\Delta S_1 = 0.44\Delta Q_{24}$ (cf. ref 1). Rewriting S_1 in terms of Cartesian displacement coordinates $\Delta S_1 = 2\Delta r_1 = 2\Delta r_2 = 2\Delta r_3 = 2\Delta r_4$ yields the actual equilibrium distance changes of the Co–N bond axes. From the fit to the experimental spectrum (cf. Figure 4), this change is calculated for both compounds to be $\Delta r_i = 0.06$ Å. Since F_{S_1} and also F_{24} are negative,[1] the normal-coordinate change is $\Delta Q_{24} > 0$. The molecule in the lowest excited singlet state ^1B_g is therefore expanded along the Q_{24} coordinate, which essentially amounts to a Co–N bond lengthening. This is reasonable since this ligand field transition involves promotion of an electron from weakly antibonding π orbitals (t_{2g}) to strongly antibonding σ orbitals, which decreases the metal–ligand bond strengths.

The treatment above is based on the assumption that the normal coordinates of the electronic excited state Q' have

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Table II. Vibrational Frequencies and Potential Energy Distributions Obtained from a Normal-Coordinate Analysis Carried Out for a Molecule of *trans*-$[Co(CN)_2(N^*{}_2C^*{}_2H_4)_2]^a$

	H freq/cm^{-1}		D freq/cm^{-1}		
vib mode	obsd	calcd	obsd	calcd	PED/%
$\nu_1(b_u)$	2138	2129	2138	2129	ν_a(CN) 95, ν_a(CoC) 5
$\nu_2(a_g)$		2129		2129	ν_s(CN) 95, ν_s(CoC) 5
$\nu_3(a_g)$		961		942	ν_s(NC) 66, ν_s(CC) 26
$\nu_7(a_g)$		755		744	ν_s(CC) 66, ν_s(NC) 18, δ(CoNC) 9
$\nu_9(b_u)$	598	602	566	584	δ(NCC) 45, ν_a(CoN) 24, δ(NCoN) 13
$\nu_{11}(b_u)$	540	548	533	542	ν_a(CoC) 86, δ(NCoC) 12
$\nu_{12}(a_g)$	523	511	493	503	δ(NCoC) 48, δ(CoCN) 29
$\nu_{13}(a_u)$	503	502	498	482	ν_a(CoN) 84, δ(NCC) 9
$\nu_{14}(a_g)$		487		464	ν_s(CoN) 47, δ(NCC) 13, δ(CoNC) 10, δ(NCoC) 9, δ(CoCN) 8
$\nu_{15}(b_u)$	458	450	450	440	ν_a(CoN) 66, δ(NCC) 24
$\nu_{16}(a_u)$	440	420	420	413	δ(NCoC) 38, δ(NCoN) 33, δ(NCC) 12
$\nu_{17}(a_g)$	424	409	400	407	ν_s(CoC) 85, δ(NCC) 4
$\nu_{19}(a_g)$		374		366	C–C tors 21, N–C tors 20, ν_s(CoN) 17, δ(CoCN) 12
$\nu_{23}(a_u)$	314	314	287	308	δ(NCoC) 68, δ(NCC) 18, δ(NCoN) 12
$\nu_{24}(a_g)$	269	276	267	271	δ(NCoN) 44, ν_s(CoN) 15, δ(CoNC) 14, ν_s(NC) 9, C–C tors 8, N–C tors 5
$\nu_{27}(a_g)$		201		197	δ(CoCN) 47, δ(NCoC) 42

[a] N* is substituted for NH_2 and ND_2, respectively, and C* for CH_2 (see text).

shifted origins (and the corresponding normal modes different frequencies) but are otherwise parallel to the normal coordinates of the ground state Q_i. A significant problem that has not been considered here and elsewhere in the literature that deals with vibronic band analyses is mode mixing. Since the normal-coordinate analysis yields similar S_1 symmetry coordinate contributions to several Q_i (i = 12, 14, 19, 24) normal coordinates, cross terms $\langle A_{1,ij}\rangle_{nd}Q_iQ_j$ (i, j = 12, 14, 19, 24) become important in the dynamical metal–ligand potential for the nuclear motion.[15] The matrix elements $\langle A_{1,ij}\rangle_{nd}$ are derivatives of the ligand field potential with respect to Q_i and Q_j at the equilibrium configuration of the nuclei, averaged over the radial parts of the *nd* functions. Thus, the normal modes Q_i (i = 12, 14, 19, 24) are not separated; in other words, they are rotated in excited electronic states compared to the ground state (i.e. the Dushinsky mixing).[14] The relationship between the Q_i' and the symmetry coordinates is, in matrix notation, $S = \mathbf{L}(\mathbf{W}^{-1}Q'-Q)$, where **W** is the rotational matrix. The line shape must then be calculated for nonseparable vibrations replacing in eq 1 the one-dimensional intramolecular distribution, $I_1(n)$, by a multidimensional intramolecular distribution (MDID), i.e. by $I_4(\{n_i\})$ in the present case.[16] The function depends on the set of spectroscopic parameters $\{\Delta_i\}$ and $\{\beta_i\}$ (i = 12, 14, 19, 24), upon the frequency ratios of the modes β_{ij}, and upon the rotational angles as well. A calculation of these line shapes reveals two main characteristics of the vibronic structure:[16] in general, a large amount of vibrational structure is present, for which the identification of different distorting (accepting) modes is difficult (scrambling effect); however, for distinct values of rotational angles a single mode progression can occur. Such single progressions are not expected from the coupling between an electronic transition and more than one molecular vibration, but they become a characteristic feature for certain normal-coordinate rotations.

Since the observed spectrum of the present cobalt compound can only be explained by a single progressional mode, the line shape function either contains the intramolecular distribution $I_1(n)$ for parallel transformations of the normal modes $Q_i \rightarrow Q_i'$ or, which cannot be ruled out, involves a MDID, $I_4(\{n_i\})$, at a specific set of rotations of these coordinates.

Concluding Remarks. Several investigations have been carried out in order to explain the vibrational fine structure of ligand field absorption and emission spectra associated with the $t_{2g} \rightarrow e_g$ (in O_h) transition in transition-metal complexes containing unidentate ligands, e.g., halides and amines.[1,8] The fit of the vibronic spectrum and a normal-coordinate analysis demonstrates that the electronic excited-state conformation undergoes a change in geometry relative to the ground state. In the D_{4h} *trans*-$[Co(CN)_2(NH_3)_4]^+$ complex, this distortion amounts to an expansion in the Co–N bond length by about 0.1 Å and a considerably smaller change along the fourfold axis. The forces changing the energy of the $^1A_{2g} \leftarrow {}^1A_{1g}$ excitation act only in the CoN_4 plane, because of the axial symmetry of the corresponding dynamical ligand field. Similar forces can be assumed for the present C_{2h} chelate complex, since changes in the electronic structure are predominantly due to certain d-orbital transitions that are similar for both complexes.

In this context it is worth noting the relation to other work on chelate complexes. Denning and Dingle et al.[2] have observed in the absorption and circular dichroism spectra of $[Co(en)_3]^{3+}$ (transition $^1T_{1g}(O_h) \leftarrow {}^1A_{1g}$) a progression in a 250-cm^{-1} mode. Flint et al.[17] have suggested that the Raman-active vibration of $[Co(en)_3]^{3+}$ at ca. 260 cm^{-1}, to which the progressional interval should be assigned, must involve larger Co–N stretching character than the band at ca. 500 cm^{-1} assigned to ν(Co–N). Although these findings agree with the general concept that electronic transitions into an antibonding orbital, $t_{2g} \rightarrow e_g$, must result in an expansion of the metal–ligand bonds, Borch et al.[12] have criticized this statement on the basis of the calculated potential energy distributions (PED) in their normal-coordinate analysis of $[Rh(en)_3]^{3+}$. Recently, it has been concluded from the spectra of some octahedral transition-metal d^6 complexes[8,18] that the electronic excited state of orbital symmetry T_1 undergoes a large Jahn–Teller distortion ($T \times e$ coupling) during excitation, in addition to a totally symmetric expansion of the complex. Therefore, an analysis of the vibrational structure of the ligand field bands of the $[Co(en)_3]^{3+}$ chelate complex must consider the competing intramolecular forces and the various contributions to the normal modes of vibration. In addition, the difficulties of possible mode mixing cannot be neglected.

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