polarizations would be vibronically induced. While an MO diagram (Figure 1) places it at about the same energy[3c] as $\delta \rightarrow \delta^*$, proper account of electron repulsion[24] could lead to a shift to higher energy of the required magnitude. The ~630-nm band is the lowest energy candidate for $\delta \rightarrow \pi^*$ according to our near-infrared results.[8] Excitations such as $\pi \rightarrow \delta^*$ are also plausible candidates but would be expected[6b] at higher energy.

We finally consider the intense z-polarized absorption, $\lambda_{max} \simeq$ 460 nm. Norman et al.[3c] have assigned this transition to $6e_u \rightarrow 6e_g$ (Figure 1). Since no vibronic structure was observed for this band, we can only note that the observed $\|z$ polarization is consistent with this assignment. One puzzling feature is that resonance Raman spectra for excitation into this band show patterns of ground-state vibrational intensification[21] that are similar to the vibronic intensity pattern seen for the $\delta \rightarrow \delta^*$ transition[8] and also to Raman spectra observed for $\delta \rightarrow \delta^*$ excitation of other compounds;[6a] namely, long progressions in $\nu(M_2)$ are observed. The $\delta \rightarrow \delta^*$ excitation is calculated[3c] to be a rather pure metal–metal transition, whereas interaction between metal–metal and carboxylate orbitals of e_u symmetry results in the calculated $6e_u$ orbital having a great deal of carboxylate character. So $6e_u \rightarrow 6e_g$ is expected to have LMCT character, according to the calculation, whereas the resonance Raman data suggest a pure metal–metal $\pi \rightarrow \pi^*$ transition. There is not, however, necessarily any contradiction here, as relaxation effects might result in the excitation being more metal–metal-localized than ground-state orbitals suggest. In any case, this is the lowest energy excitation of the $\pi \rightarrow \pi^*$ type.

Intensities of Metal–Metal Transitions

From the data for monochloro and dichloro $Ru_2(O_2CPr)_4^+$ complexes (Table I), we estimate oscillator strengths for the $\delta \rightarrow \delta^*$ transition of 0.0006 and 0.0009, respectively. The intensity of the transition increases as the energy of axial LMCT decreases (Table I), which we attribute to a small degree of mixing between these two molecular z-polarized transitions.

The oscillator strength of the ~23 000-cm^{-1} band of $Mo_2(O_2CH)_4$ that is now[7] assigned as $\delta \rightarrow \delta^*$ has been estimated[3a] to be 0.0008. Thus, the intensity of $\delta \rightarrow \delta^*$ is not very sensitive to metal–metal bond length and/or bond order for these carboxylate-bridged complexes. The large shift in $\delta \rightarrow \delta^*$ energy between the Mo_2 and Ru_2 complexes is not predominantly a one-electron effect, but instead results from differences in electron repulsion contributions[6,24,25] to the transition energy for $\delta^2(\delta^*)^0$ and $\delta^2(\delta^*)^1$ ground-state configurations; the two-electron terms roughly cancel out for $\delta^2(\delta^*)^1$.

The low oscillator strengths[26] and $\nu(M_2)$ Franck–Condon factors indicate[27] that the δ-symmetry metal–metal interaction must be very weak, and as discussed in detail elsewhere,[3,25] much of the δ/δ^* splitting is attributable to interaction of carboxylate orbitals with the δ/δ^* orbitals, rather than to direct metal–metal interaction.

We finally note that the only other well-established example of a metal–metal $\pi \rightarrow \pi^*$ transition is that of $Re_2X_8^{2-}$; it is assigned to an intense ($f \simeq 0.2$) band at 38 000 cm^{-1}. That its intensity is so much greater than that of the lowest $\pi \rightarrow \pi^*$ transition of the ruthenium carboxylates (~22 000 cm^{-1}, $f \simeq 0.02$) presumably reflects some combination of mixing with halide-to-metal CT transitions (analogous to that required[25] to explain the relatively high intensity of the $\delta \rightarrow \delta^*$ transition of $Re_2Cl_8^{2-}$), stronger metal–metal π-bonding, and differing metal–metal character in the electronic transition.

Acknowledgment. We thank Don Martin and Steve Rice for helpful discussions. This research was supported by National Science Foundation Grant CHE84-19828.

Registry No. PMMA, 9011-14-7; $[Ru_2(O_2CH)_4Cl_2]^-$, 71767-76-5; $Ru_2(O_2CPr)_4Cl$, 47511-63-7; $[Ru_2(O_2CPr)_4Cl_2]^-$, 114595-61-8; $[Ru_2(O_2CPr)_4Br_2]^-$, 114595-62-9; $[Ru_2(O_2CPr)_4I_2]^-$, 114595-63-0; $Ru_2(O_2CMe)_4Cl$, 38833-34-0; $Ru_2(O_2CEt)_4Cl$, 71061-91-1; $Ru_2(O_2CPr)_4Br$, 107053-30-5; $Ru_2(O_2CPr)_4^+$, 114691-50-8.

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Electronic and Raman Spectra of the Linear NiO_2^{2-} Ion in K_2NiO_2

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The polarized spectrum of a single crystal of K_2NiO_2 is reported over the range 3000–22 500 cm^{-1} and assigned on the basis of a ligand field calculation. The d-orbital energies imply significant configuration interaction between the metal $3d_{z^2}$ and 4s orbitals in the linear NiO_2^{2-} ion. Vibrational fine structure in the optical spectrum suggests that in the $^3\pi_g$ excited state the energy of the totally symmetric stretching vibration decreases significantly from the ground-state value observed in the Raman spectrum, and this is correlated with the expected increase in the equilibrium Ni–O bond length. The extreme dichroism of the band in the visible region may be explained by considering the nature of the two electronic states involved in the transition and the form of the intensity-inducing vibrations.

Introduction

The electronic spectra of numerous tetragonally distorted nickel(II) complexes have been reported,[1] and these have frequently been used to test models of the bonding in transition-metal compounds.[2] However, such compounds have usually involved a tetragonal weakening of the ligand field, with the extreme limit of this kind of distortion producing a square-planar geometry. These planar metal complexes are unusual because it is impossible to explain their energy levels satisfactorily without including the higher energy metal s orbital in the bonding scheme.[3,4] Just as

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(1) For a comprehensive listing of the spectra of tetragonal nickel(II) complexes see: Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; Chapter 6.

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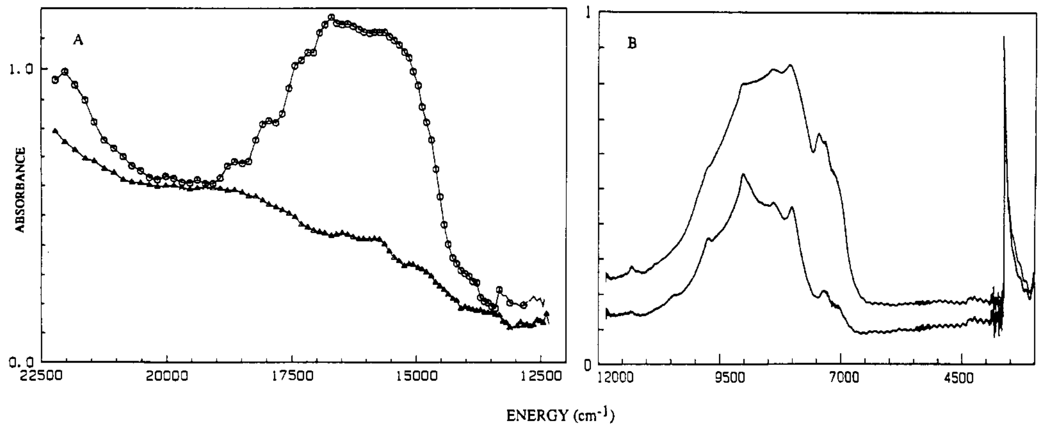

Figure 1. Electronic spectrum of a single crystal of K_2NiO_2 of thickness 0.01 cm with the electric vector parallel (‖) and perpendicular (⊥) to the [001] direction. Region A was recorded manually by using a Leitz microspectrophotometer, while B was measured with a Digilab FTS-40 near-infrared spectrometer.

Table I. Observed and Calculated Peak Positions (cm^{-1} × 10^{-3}) and Tentative Band Assignments for the Electronic Spectrum of K_2NiO_2

	peak energies and tentative band assignments					
	$3\Delta_g$, $3\ \Sigma_g$	$^1\Sigma_g$	$^3\Phi_g$	$^1\Sigma_g$	$^1\Delta_g$	$^3\Pi_g$
obsd	*a*	7.1,[b] 7.325,[b] 7.47	8.04, 8.42, 9.05, 9.78	11.275	13.50	15.59, 16.16, 16.71, 17.36, 17.99, 18.63, 19.31, 19.95
calcd	2, 48, 2.95, 3.26, 3.35, 3.39	7.14	8.29, 8.95, 9.50	11.48	13.89	15.43, 15.46, 15.68, 15.71

[a] Region below 3000 cm^{-1} not investigated. [b] Weak shoulder.

axial elongation of an octahedron leads to a planar geometry, so axial compression produces a linear structure in the limit that the in-plane ligands are lost from the coordination sphere. In fact, these ligand displacements are equivalent to the two possible Jahn–Teller distortions of a complex with a doubly degenerate electronic state, and to first order they are expected to have similar effects on the e_g orbitals except that $d_{x^2-y^2}$ and d_{z^2} are interchanged. Recently, we prepared the compound K_2NiO_2 and showed that it contains linear NiO_2^{2-} ions.[5] This therefore provides a good opportunity to study the spectroscopic properties of Ni^{2+} in the unusual linear coordination geometry, for comparison with those in the more common planar arrangement.

Experimental Section

The preparation of crystals of K_2NiO_2 has been described previously.[5] The crystals are very hygroscopic and were therefore sealed into quartz tubes before spectral measurements were made. Electronic spectra in the region 3000–12000 cm^{-1} were recorded with polarized light by using the near-infrared version of a Digilab FTS-40 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled InSb detector. The crystals were mounted under an Digilab microscope, and a sample area of 50 × 150 mm was selected by using the variable microscope aperture. In the region 12000–22500 cm^{-1} spectra were recorded by using a Leitz MPV2 microscope photometer connected to an Optica monochrometer. The wavelength was stepped by hand in intervals of 0.5 nm. In both wavelength ranges the reproducibility of the results was checked by recording the spectra of two separate crystals. The dimensions of the crystal used to measure the spectrum shown in Figure 1, measured by using a microscope eyepiece with a graduated scale (1 division = 0.0164 mm), were as follows: length, 0.020 cm; width, 0.013 cm; thickness, 0.010 cm. As the density of K_2NiO_2 is 2.796 g/mL,[5] for this crystal an optical density of 1 corresponds to a molar extinction coefficient of ~6 M^{-1} L cm^{-1}. The diameter of the tube containing the crystals was 0.035 cm so that the curvature of the tube was small over the aperture width (0.005 cm) used to measure the spectra. The Raman spectrum of a crystal was measured in the range 50–1200 cm^{-1} on a Cary 18 spectrophotometer using the 514.5-nm excitation line of an Ar laser. All measurements were made at room temperature.

Results and Discussion

The compound K_2NiO_2 crystallizes with a tetragonal unit cell containing linear NiO_2^{2-} units aligned parallel to the [001] crystal axis. The closest contacts in the *xy* plane are with neighboring Ni^{2+} ions at 3.953 Å, so that the metal is truly 2-coordinate.[5] Typical electronic spectra with the electric vector parallel and perpendicular to this axis are shown in Figure 1. The sharp peak at 3500 cm^{-1} is assigned as the OH stretching peak of a small amount of hydroxide in the quartz sample tube. The rest of the spectrum, which is assigned to "d–d" transitions of the Ni^{2+} ion, consists of broad, structured bands centered at ~9000 and ~16000 cm^{-1}, the latter band being virtually completely polarized parallel to the O–Ni–O axis. Individual peak positions and the overall band assignments are given in Table I.

Polarization of the Band in the Visible Region. As the complex is centrosymmetric, the "d–d" transitions are Laporte forbidden and the intensity is derived from higher energy charge-transfer states via coupling with ungerade vibrations. In agreement with this the band intensities are quite low ($\epsilon \approx 5$ M^{-1} L cm^{-1}), being similar to those observed for other centrosymmetric Ni^{2+} complexes formed by oxygen ligands.[1] It might be thought that the absence of the band at ~16000 cm^{-1} in *xy* polarization can be explained by using vibronic selection rules and that this could help assign the spectrum. However, inspection of the direct products of the characters of the point group of the complex ($D_{\infty h}$) shows that a vibration is available to induce intensity in the transition for each possible ground state of the complex[6] and the same is true even if the crystallographic site symmetry of the Ni^{2+} (D_{4h}) is used to derive the vibronic selection rules. Another possible cause of the strong dichroism of the band might be the dominance of a single *z*-polarized charge-transfer transition in the intensity-stealing process. A mechanism of this kind has been proposed to explain the *y* polarization of the spectra of bis(acetylacetonato)copper(II) complexes.[7] However, a similar mechanism cannot apply for K_2NiO_2, as it requires that the whole spectrum is more intense in one polarization than the other, which is not the case. The assignment of the spectrum was therefore made

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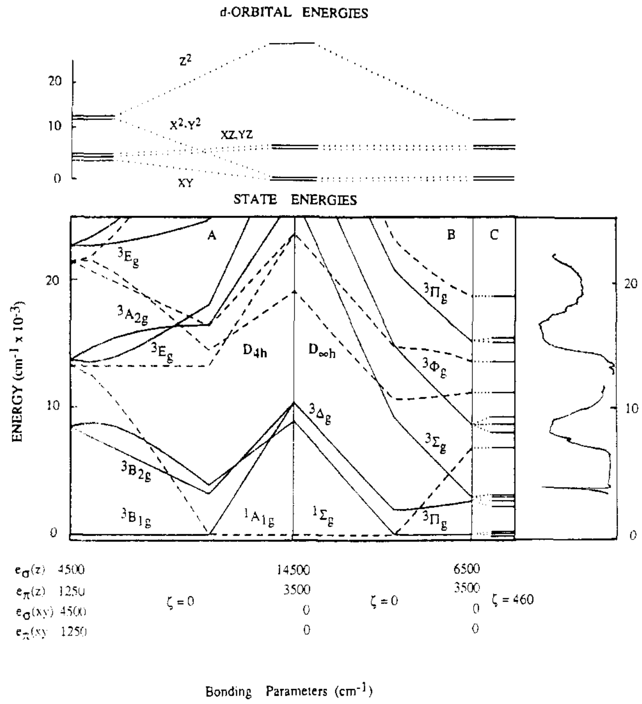

Figure 2. Change in d-orbital and state energies that occur as a Ni^{2+} complex distorts from an octahedral to linear geometry (region A), followed by a progressive decrease in the d_{z^2} orbital energy (region B), with the effect of spin–orbit coupling being shown in region C. The angular overlap metal–ligand bonding parameters are shown for the limiting situations, as are the band positions observed in the electronic spectrum.

solely on the basis of ligand field calculations described below.

The very low intensity of the band at ~16 000 cm^{-1} in *xy* polarization may, however, be explained by considering the relative effectiveness of the *u*-vibrational modes inducing intensity. According to conventional theory,[1] the intensity of the "d–d" transitions of centrosymmetric complexes is derived from the vibronic admixture of ligand and, to a lesser extent, metal p orbitals into the molecular orbitals involved in the transitions. Ligand displacements along normal coordinates that remove the inversion center of the complex may produce nonzero transition moment integrals between metal d and ligand p wave functions. According to the present assignment (Figure 2), the $^3\pi_g$ ground state of K_2NiO_2 corresponds to the electron configuration $(xy, x^2 - y^2)^4(xz, yz)^3(z^2)^1$ while the band at ~16 000 cm^{-1} is due to a transition to the $^3\pi_g$ excited state corresponding to the electron configuration $(xy, x^2 - y^2)^3(xz, yz)^3(z^2)^2$. The transition thus involves the excitation of an electron from the nonbonding $(xy, x^2 - y^2)$ orbitals to the σ-antibonding (z^2) orbital. To a good approximation neither of the *u*-vibrational modes of the NiO_2^{2-} ion, pictured in Figure 3, will mix ligand p orbitals into the nonbonding $(xy, x^2 - y^2)$ orbitals, so that the intensity of this particular transition must be derived entirely from integrals involving the ground-state d orbitals and p functions mixed into the excited-state (z^2) molecular orbital. However, only the stretching mode of Σ_u symmetry will produce changes in the coefficients of the p orbitals that will give rise to integrals of this kind (see Figure 3). While a displacement along the Π_u bending coordinate will slightly decrease the oxygen p contribution to the z^2 molecular orbital, this will occur in a symmetrical fashion and so will not give rise to any nonzero transition moment integrals. Since the intensity of the $^3\pi_g \leftarrow {}^3\pi_g$ transition in *z* polarization is induced by the Σ_u vibration, while that in *xy* polarization is produced by the Π_u vibration, the inactivity of the latter vibration predicted by the above arguments provides a good explanation of the extremely low intensity of the band at ~16 000 cm^{-1} in *xy* polarization. It may be noted that the band at ~9000 cm^{-1} is assigned as the transition to the $^3\Phi_g$ state, which involves the excitation from the *xz*, *yz* orbitals to the z^2 molecular orbital. In view of the strong π-bonding in the NiO_2^{2-} ion, both *u*-vibrations are expected to produce a significant admixture of ligand p orbitals into the (xz, yz) ground-state molecular orbital, so that intensity may be induced into the $^3\Phi_g \leftarrow {}^3\pi_g$ transition in both *xy* and *z* polarization, in agreement with experimental observation (Figure 1).

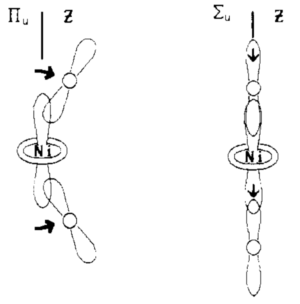

Figure 3. Ungerade vibrational modes of the NiO_2^{2-} ion.

Metal–Ligand Bonding Parameters. The Angular Overlap Model (AOM) has proved a particularly fruitful method of describing the bonding in transition-metal complexes.[8] We recently used the computer program CAMMAG, written by Gerloch and co-workers,[9] to successfully interpret the electronic spectra and magnetic properties of a number of complexes with novel structures within the framework of this model,[10] and a similar approach was applied to the present problem. The starting point of the calculations were estimates of the AOM bonding parameters in cubic NiO:$e_\sigma \approx 4500$ cm^{-1}, $e_\pi \approx 1250$ cm^{-1} obtained from the observed d-orbital splitting ($\Delta = 8900$ cm^{-1})[11] by using the expression $\Delta = 3e_\pi - 4e_\pi$ appropriate for a regular octahedral complex and the relationship $e_\sigma = 4e_\pi$, which has been deduced for π-bonding ligands such as oxide.[8,12] The effect of the distortion from octahedral to linear geometry was described initially by progressively decreasing the bonding parameters of the in-plane ligands to zero, while at the same time increasing those of the axial ligands by assuming that they depend inversely on some power *n* of the bond length. For NiO, Δ has been observed to increase in this way when the bond length shortens under the application of high pressure,[11] with *n* lying between 5 and 6, and it has been pointed out that this is in agreement with theory.[13] The Ni–O distance in NiO is 2.10 Å,[14] and in K_2NiO_2 this decreases to 1.687 Å.[5] Because of the large change in bond length, the above relationship can be expected to give only an approximate guide to the energy levels of the NiO_2^{2-} ion, though it may be noted that the d-orbital splittings in the octahedral and planar (acetylacetonato)nickel(II) complexes, where the Ni-O distances change from ~2.09[15] to 1.836 Å,[16] do show a relationship of just this kind (Δ changes from 8800[17] to ~18 500 cm^{-1} [18]). The changes calculated in this manner for the linear NiO_2^{2-} ion, with e_σ increasing to 14 500 cm^{-1} and e_π to 3500 cm^{-1}, are shown in Figure 2A for both the d-orbital and state energies. The latter were obtained by including the effects of interelectron repulsion using the Condon–Shortley pa-

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rameters $F_2 = 1288.8$ cm^{-1} and $F_4 = 112.0$ cm^{-1}.

At this stage, the calculation not only suggests energy levels giving poor agreement with the observed spectrum, it also implies that the compound is low spin, in contrast to experiment, which has shown K_2NiO_2 to be paramagnetic.[19] The most important deficiency in the model is the neglect of configuration interaction between the metal 4s and $3d_{z^2}$ orbitals. This is known to depress the $^1A_{1g}(z^2)$ state by ~6000 cm^{-1} in planar Ni^{2+} compounds,[3] and the effect should be even larger in a linear complex.[4] The effect of progressively lowering the energy of the d_{z^2} orbital by decreasing e_σ to 6500 cm^{-1} is shown in Figure 2B. This not only produces a paramagnetic ground state, as observed, but also excited-state energies in reasonable agreement with the observed transition energies, particularly when spin–orbit coupling is included (Table I, Figure 2C). The proposed assignment, with a $^3\pi_g$ ground state, and the bands at ~9000 and ~16 000 cm^{-1} being due to transitions to the $^3\Phi_g$ and $^3\pi_g$ excited states, respectively, is consistent with that proposed[20,21] for linear $NiCl_2$, where the corresponding bands are observed at somewhat lower energy (~5000 and 13 000 cm^{-1})[20]. The $^3\Delta_g$ and $^3\Sigma_g$ states of NiO_2^{2-} are calculated to give rise to a set of levels between 2480 and 3390 cm^{-1} (Table I), so that these presumably give rise to transitions outside the spectroscopic range of the present study.

If the orbital reduction parameter is chosen to be reasonably consistent with the expected covalency of the complex, $k = 0.8$, the calculated magnetic moment, $\mu = 3.5\ \mu_B$, is higher than that measured experimentally,[19] $\mu \approx 3.0\ \mu_B$ (the experimental value involves a correction for a significant antiferromagnetic interaction in the complex). The high calculated value of μ occurs because of the low energy of the $^3\Delta_g$ excited state, ~2500 cm^{-1}, and it was impossible to choose bonding parameters giving lower values of μ without contradicting the optical spectrum. A value of μ equal to that observed experimentally was calculated by using the above bonding parameters and a low value of $k = 0.3$. This may indicate some quenching of the orbital angular momentum in the ground state, possibly by a Ham effect.[22] A similar value of k (0.25) was required to explain the magnetic moment of the high-spin planar FeO_4 units in gillespite,[23] where the orbital angular momentum is also derived from a low-lying excited orbital doublet.

The present model suggests that the properties of K_2NiO_2 are influenced strongly by configuration interaction between the $3d_{z^2}$ and 4s orbitals. Indeed, it seems likely that the most obvious distinction between the linear and planar geometries derived from a parent octahedral nickel(II) complex via tetragonal distortions of opposite sign, namely that the former, as exemplified by NiO_2^{2-}, are paramagnetic, while the latter are usually diamagnetic, is due to this effect. This is because the lowering of $d_z{}^2$ by d–s mixing favors a low-spin ground state for a planar compound, but stabilizes a high-spin state for a linear one. In a linear complex the d-orbital energies are related to the AOM parameters as follows:[21] $E(z^2) = 2e_\sigma$ and $E(xz, yz) = 2e_\pi$, with $E(x^2 - y^2, xy) = 0$. The optimum values for the NiO_2^{2-} ion, $e_\sigma = 6500$ cm^{-1} and $e_\pi = 3500$ cm^{-1} agree well with the estimates $e_\sigma = 4798$ cm^{-1} and $e_\pi = 3098$ cm^{-1} obtained by Lever and Hollebone[21] from the electronic spectrum of the $NiCl_2$ molecule. The value $e_\pi = 3500$ cm^{-1} suggests that the oxide ligands in NiO_2^{2-} are strong π-donors, which seems reasonable in view of the very short bond distance. In six-coordinate Ni(II) complexes with oxygen ligands e_π is typically about one-third of this value.[12] The parameter e_σ includes both the σ-antibonding interaction of the ligands and the effect of configuration interaction with the metal 4s orbital. As already mentioned, it seems likely that the latter contribution is substantial, producing a decrease in energy of the d_{z^2} orbital on an order of magnitude of ~−16 000 cm^{-1}. This is ~3 times the corresponding energy shift deduced for planar complexes of first-row transition ions.[3,23,24] Assuming that the metal 4s orbital is ~80 000 cm^{-1} above the d orbitals,[24,25] a simple perturbation calculation implies a ~20% fractional electron occupancy of this orbital in the half-filled $\Sigma_g(z^2)$ orbital, which is consistent with the value of ~25% suggested by the analysis of the hyperfine splittings observed in the EPR spectrum of the linear CuF_2 molecule.[26]

Raman Spectrum. The Raman spectrum of K_2NiO_2 shows a single sharp peak centered at 732.5 cm^{-1}, which may be assigned to the ν_1 totally symmetric stretching vibration of the NiO_2^{2-} ion (the other two modes are Raman inactive). This implies a high force constant for the Ni–O bonds (5.06 mdyn Å^{-1}), comparable to that in tetrahedral oxyanions such as MnO_4^- (6.65 mdyn Å^{-1})[27] and much higher than in an octahedral Ni^{2+} complex such as $Ni(H_2O)_6^{2+}$ (1.74 mdyn Å^{-1}).[28] If it is assumed that the force constant is inversely proportional to some power n of the bond distance, then the increase from 1.74 to 5.06 mdyn Å^{-1}, which accompanies the shortening of the Ni–O bonds from 2.06 Å in $Ni(H_2O)_6^{2+}$[29] to 1.687 Å in K_2NiO_2 implies a value of $n \approx 5.3$. It is interesting to note that a power dependence of this kind ($n \approx 5$) is predicted theoretically for the variation of the d-orbital splitting as a function of metal–ligand bond length.[13]

Fine Structure. The spectrum exhibits considerable fine structure (Figure 1). The weak, sharp peaks at 11 275 and ~13 500 cm^{-1} are assigned as spin-forbidden transitions. While it seems clear that the structured band covering the region 7000–10 000 cm^{-1} is due to transitions to the $^1\Sigma_g$ and $^3\Phi_g$ excited electronic states, an unambiguous assignment of the individual peaks is impossible. The calculations suggest that spin–orbit coupling splits the $^3\Phi_g$ state into three approximately equally spaced levels, with a total energy separation of ~1200 cm^{-1} (Table I). A tentative assignment ascribes the peaks at ~7100, 7325, and 7470 cm^{-1} to transitions to the $^1\Sigma_g$ state coupled to low-energy vibrations (these could be either lattice modes, or the ν_3 bending vibration, which is likely to have a very low energy). The relatively high intensity of the 7490-cm^{-1} peak is not unreasonable considering its close proximity to the spin-allowed transition at 8040 cm^{-1}. The peaks at 8040, 8420, and 9050 cm^{-1} are assigned to the spin–orbit components of the $^3\Phi_g$ state, with the energy separation to the following peak at 9780 cm^{-1} (730 cm^{-1}) suggesting that this could be due to the additional excitation of a quantum of the totally symmetric ν_1 vibration. An alternative, marginally less attractive assignment ascribes the weak shoulders at 7100 and 7325 cm^{-1} to the $^1\Sigma_g \leftarrow {}^3\pi_g$ transition, the peaks at 7470, 8040, and 8420 cm^{-1} to transitions to the $^3\Phi_g$ state, and the 9050- and 9780-cm^{-1} peaks to a progression in the ν_1 mode.

The broad band centered at ~16 000 cm^{-1} is assigned to the $^3\pi_g \leftarrow {}^3\pi_g$ transition. As the spin–orbit splitting of the $^3\pi_g$ excited state is calculated to be quite small (~300 cm^{-1}, see Table I), this may explain why the spin–orbit components are unresolved in this band, which consists of a single, regular progression of interval ~625 cm^{-1} (Table I). This progression is apparently in the ν_1 vibration, of energy 732.5 cm^{-1} in the ground state. A decrease in energy in the excited state is expected for this mode, as to a good approximation an electron is being promoted from the nonbonding d_{xy}, $d_{x^2-y^2}$ orbital to the antibonding d_{z^2} orbital. The equilibrium Ni–O bond length should therefore increase in the $^3\pi_g$ excited state, and this will have the effect both of lowering the vibrational frequency and of causing a band in the totally symmetric mode. If, as discussed above, the force constant varies

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as about the fifth power of the bond length, the observed decrease in the vibrational energy implies a bond length of ~1.80 Å in the $^3\pi_g$ excited state.

The increase in bond length in the excited state may also be calculated from the relative intensities of the components of the band,[30] but in the present case, these are not well enough resolved to warrent such an analysis. However, we recently described[31] a simple relationship by which the bond length change δr accompanying an electronic transition may be estimated from the force constant f of the ν_1 vibration, if it is assumed that the energy difference Δ between the d orbitals involved in the transition depends inversely on some arbitrary power n of the bond length:

$$\delta r \approx \Delta nm/(frN)$$

Here, N is the number of ligand atoms (2 in the present case) and m is the number of electrons involved in the transition. This expression has been found to give good agreement with the bond-length changes derived from the analysis of the electronic spectra of a wide range of complexes[30,31] with a value of $n \approx 5$. To a good approximation, for the $^3\pi_g \leftarrow {}^3\pi_g$ transition, a single electron is promoted from the d_{xy}, $d_{x^2-y^2}$ to the d_{z^2} orbital, and substitution of the value $m = 1$ and $\Delta = 13\,000$ cm^{-1} into the above equation, together with $n = 5$, $r = 1.687$ Å, and $f = 5.06$ mdyn Å^{-1} = 2.55 × 10^5 cm^{-1} Å,$^{-2}$ suggests that each Ni–O bond length should increase by a total of $\delta r \approx 0.0755$ to ~1.76 Å in the $^3\pi_g$ excited state, in fair agreement with the above estimate derived from the decrease in the bond force constant.

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EPR Reinvestigation of the Copper(II)–Imidazole System

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An EPR reinvestigation of the copper(II)–imidazole system has been carried out. The room-temperature EPR spectrum recorded with a low molar ratio, [Cu^{2+}]:[imidazole] = 1:10, reveals the features of two absorbing species, probably [Cu(imidazole)$_3$]$^{2+}$ and [Cu(imidazole)$_4$]$^{2+}$. The experimental results at high molar ratios at both room and low temperatures give evidence of the formation of a well-characterized four-coordinated species, [Cu(imidazole)$_4$]$^{2+}$. A critical comparison with a recent report in which EPR parameters have been attributed to [Cu(imidazole)$_5$]$^{2+}$ and [Cu(imidazole)$_6$]$^{2+}$ is also made.

Introduction

Recently an EPR characterization of the various species present in the copper(II)–imidazole (imH) system and analogous complexes as well as some mixed complexes having imH as the second ligand has been reported.[1] However, we have set little value on the conclusions reached by the authors of that paper for the following reasons.

(i) They assigned EPR spectra to [Cu(imH)$_n$]$^{2+}$ (n = 4–6) complexes, without having determined the species distribution in the copper(II)–imidazole system; accordingly, the copper–imidazole (and –methylimidazole as well) complexes reported in their paper were not those the authors thought to be present in solution.

(ii) Their hypothesis on the formation of a pentakis(imidazole)copper(II) species was based on the shifts undergone by $g_\parallel$ and $A_\parallel$ values with respect to those of a presumed tetrakis complex; the changes of the magnetic parameters should have been the opposite of those reported.

(iii) Although their EPR spectra showed a well-resolved shf structure, it only appeared in the perpendicular region; furthermore, on the basis of 11 shf lines, they deduced the pentakis(imidazole)copper(II) complex formation, while it is well-known that apical nitrogens contribute to shf interaction in a way different from those bound in the equatorial plane.

(iv) They tried to rationalize trends in rhombic distortion among a series of copper–amine and –polyamine complexes, the EPR spectra of which are essentially axial; they mistook an extra peak for a different resonance line with a peculiar g value.

Therefore, we decided to undertake an EPR reinvestigation of the copper(II)–imidazole system both in water–methanol and in water–dimethyl sulfoxide (Me_2SO) mixtures, the latter mixture being that used in the previous paper.[1]

Experimental Section

$^{63}CuSO_4$ was purchased from Stable Isotope Unit Chemistry Division, Harwell, Oxfordshire, England, and imidazole (Fluka, purissimum) was recrystallized twice from benzene. Twice-distilled water and reagent grade methanol and dimethyl sulfoxide were used to prepare the complex solutions. Three different ratios, [Cu^{2+}]:[imH] = 1:10, 1:100, and 1:200, were used, the concentration of copper(II) ions being 5 × 10^{-3} mol dm^{-3}. To adjust the solution pH to a value of about 7, imidazole (pK = 7.03) was neutralized up to 50% by adding HNO_3. The calculations associated with the species distribution in the copper(II)–imidazole system have been carried out by using the program DISDI.[2] To get the species distribution as a function of pH, we used the values of log β_n (n = 1–4) reported by James et al.:[3] log β_1 = 4.33, log β_2 = 7.61, log β_3 = 10.31, and log β_4 = 12.2.

EPR spectra were recorded with a conventional X-band spectrometer, Bruker ER 200 D, equipped with a low-temperature control unit. DPPH (g = 2.0036) was used to calibrate the klystron frequency, the magnetic field being continuously measured by means of a Model ER 035 M gauss meter, which gives markers at preselected values. Magnetic parameters were calculated by using a program substantially devised by Pilbrow et al.,[4] which allows one to deal with the shf interaction of one, two, or four nitrogen donors in the equatorial plane.

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