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Nickel(III) Complexes of 3,9-Dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione Dioxime with Two Axial Halide Ligands. ESR Spectra, Electronic Spectra, and Ligand-Exchange Kinetics

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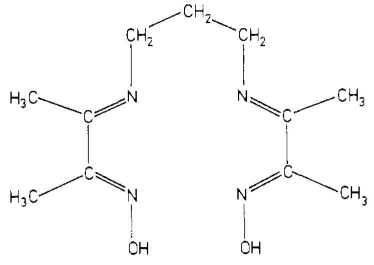
The uncharged complexes NiX_2L, with L being the anion of 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime and X = Cl or Br, were synthesized by oxidation of the corresponding Ni(II) complexes with persulfate. The complexes are soluble in dichloromethane. ESR spectra are observed in fluid solutions at room temperature, showing resolved hyperfine structure from Br and Cl nuclei ($A_{iso}(Br) = 69 \times 10^{-4}$ cm^{-1}, $A_{iso}(Cl) = 13.8 \times 10^{-4}$ cm^{-1}). Anisotropic ESR parameters are determined from spectra measured in frozen solutions or in magnetically diluted single crystals with CoX_2L as host lattices. For $NiBr_2L$ one component of the hyperfine tensor of ^{61}Ni is determined from an isotopically enriched sample. From the ESR spectra a ground state with the single unpaired electron in the d_{z^2} orbital is deduced. Near-IR/vis spectra show two weak absorptions at 9300/14 800 cm^{-1} for $NiBr_2L$ and 10 000/14 800 cm^{-1} for $NiCl_2L$, which are assigned to d–d transitions to the two lowest excited doublet states. The halide ligands are labile. The cross-exchange equilibrium $NiBr_2L + NiCl_2L \rightleftarrows 2NiBrClL$ is completely established in dichloromethane/tetrachloromethane solutions at −70 °C after $t < 1$ min. No halide exchange takes place in the reaction $NiX_2L + CoY_2L \nrightarrow NiXYL + CoXYL$ over a period of several days at room temperature.

Introduction

Until recently, nickel complexes in the oxidation state III were relatively scarce.[1] This is not too surprising, because the d^7 configuration is not very frequent in transition-metal chemistry in general. Several macrocyclic ligands have been shown to form complexes with Ni(III),[2] and it was our aim to investigate one such system by ESR spectroscopy and possibly by other methods in order to compare the low-spin d^7 configurations of Ni(III) and Co(II). The latter has been investigated in detail.[3] Complexes similar to the system studied by us were simultaneously investigated by other groups. The field was recently reviewed by Haines and McAuley.[4] Nickel(III) complexes are finding continued interest from different points of view in the current literature.[5-10] It was to be expected that the model we developed for the electronic structure of low-spin Co(II) complexes[3] could be directly applied to Ni(III). In the former, it was shown that the energies of the orbitals with predominantly metal character are generally as shown in Figure 1.

This scheme is found in many planar, four-coordinate complexes but also in five- and sixfold-coordinate species of Co(II).[11] The energetic proximity of four of the five d orbitals has as a consequence very low-lying doublet excited states.[3] In the case of the Co(II) complexes the electron–electron repulsion is much weaker in the quartet state (in which d_{xy} is singly occupied) than in any of the doublet states. Therefore, the high-spin configuration also corresponds to states of low energies. The Co(II) complexes thus represent a peculiar situation in which a molecular species has low-lying electronically excited states of the *same* and of *different* spin multiplicities as the ground state.[3] It is to be expected that Ni(III) complexes show larger energy separation between the d orbitals because of larger ligand field strength. The typical effects of the low-lying excited states, like large orbital contributions to the angular momentum and consequently strongly anisotropic **g** tensors, should therefore be attenuated in Ni(III) complexes as compared to those in the Co(II) species.

For the present paper, Ni(III) complexes with the anion of $(DOH)_2pn$ (I) = DOHDOpn were prepared and investigated by ESR and vis/near-IR spectroscopy. Preliminary kinetic results on ligand-exchange reactions are also communicated. ESR spectra were measured in liquid solution, in the glassy state, and from substitutional dopants in single crystals and polycrystalline samples of the corresponding Co(III) complexes. The complexes formed are invariably six-coordinate with the macrocyclic ligand forming a nearly planar arrangement and two halide ligands occupying the axial positions.



I

Experimental Section

Preparation of the Complexes. The syntheses of 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime ($(DOH)_2pn$) and its Ni(II) complex with iodide, NiI(DOHDOpn), have been described in the literature.[12,13] The Ni(III) complexes $NiCl_2$(DOHDOpn) and $NiBr_2$(DOHDOpn) have been synthesized as follows: NiI(DOHDOpn) is boiled together with an equivalent quantity of silver tosylate in water. The precipitated AgI is separated by filtration. A large excess of NaCl or NaBr (ca. 25 mol of NaX/mol of Ni complex) is added. After the solution is cooled to 0 °C, the metal ion is oxidized by careful addition of small portions of ammonium persulfate (0.6

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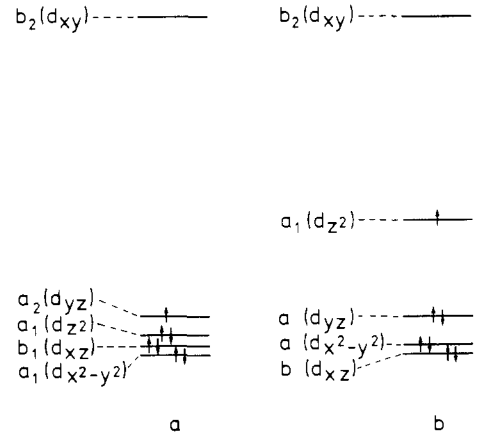

Figure 1. Relative energies of the molecular orbitals with preponderant metal 3d character of low-spin Co(II) complexes: (a) Co(acacen) as an example of 4-fold coordinated complexes; (b) Co(acacen)NH_3 as an example of 5-fold coordinated complexes.

mol of $(NH_4)_2S_2O_8$/mol of Ni complex). After ca. 1 h the Ni(III) complex is extracted with dichloromethane. The complex is precipitated by addition of tetrachloromethane. It is further purified by recrystallization from dichloromethane/methanol (yield ca. 70% after recrystallization).

Anal. Calcd for $NiBr_2$(DOHDOpn): Ni, 12.82; C, 28.86; N, 12.24; H, 4.18. Found: Ni, 12.71; C, 28.68; N, 12.09; H, 4.16. Calcd for $NiCl_2$(DOHDOpn): Ni, 15.91; C, 35.81; N, 15.19; H, 5.19. Found: Ni, 15.74; C, 35.52; N, 15.06; H, 5.12.

The same complexes were synthesized by using isotopically enriched ^{61}Ni: A 2-mg sample of the metal (88.84% ^{61}Ni, Oak Ridge National Laboratory) was dissolved in concentrated nitric acid. The excess acid was evaporated in a vacuum line; concentrated acetic acid was added and evaporated three times. The Ni(III) complexes were then synthesized as described above via NiI(DOHDOpn).

The corresponding Co(III) complexes $CoBr_2$(DOHDOpn) and $CoCl_2$(DOHDOpn) were synthesized via CoI(DOHDOpn).[14] Mixed crystals of $Co^{III}X_2$(DOHDOpn) and $Ni^{III}X_2$(DOHDOpn) were obtained by dissolving both complexes in dichloromethane followed by evaporation of the solvent under an inert atmosphere (N_2). Crystals with approximately the same Ni:Co ratio as in solution were obtained. Powder samples with 0.1%, 0.5%, 1%, 2%, and 5% Ni were sealed under vacuum in quartz tubes. Single crystals, 1–3 mm long, were grown by slow evaporation of the solvent at room temperature.

ESR Measurements. The ESR spectra were recorded on a Varian E9 spectrometer at frequencies of 9.5 GHz (X band) or 35 GHz (Q band) in the temperature range of 77 K to room temperature. At X-band frequencies g values and hyperfine splitting constants were determined by direct measurements of the magnetic field by an NMR probe and a microwave frequency counter. The Q-band frequency was determined indirectly, with use of DPPH as a standard (g = 2.0036). Solutions were measured at room temperature in flat quartz cells 0.25 mm thick. Single crystals were mounted on the bottom part of the Varian Q-band cavity with Plasticine and oriented optically on a two-circle goniometer. The angular dependence was determined by rotating the magnet. Kinetic measurements on the halogen exchange were carried out at temperatures between −70 and +20 °C by mixing two solutions in cylindrical ESR tubes within the cavity at the desired temperature. The first spectrum could be measured ca. 1 min after the mixing of the two solutions.

Vis/Near-IR Spectra. The electronic spectra of the Ni(III) complexes in dichloromethane (Fluka, puriss. p.a., spectroscopic grade) in 1-cm path length quartz cells thermostated to 20.0 °C (±0.1 °C) were recorded on a Zeiss DMR-21 spectrophotometer (4000–54 000 cm^{-1}, registration linear in wavenumber).

Results and Discussion

ESR Spectra. Both complexes $NiBr_2$(DOHDOpn) and $NiCl_2$(DOHDOpn) give in solution near room temperature well-resolved ESR spectra showing hyperfine structure from two bromine and two chlorine nuclei, respectively (Figures 2 and 3).

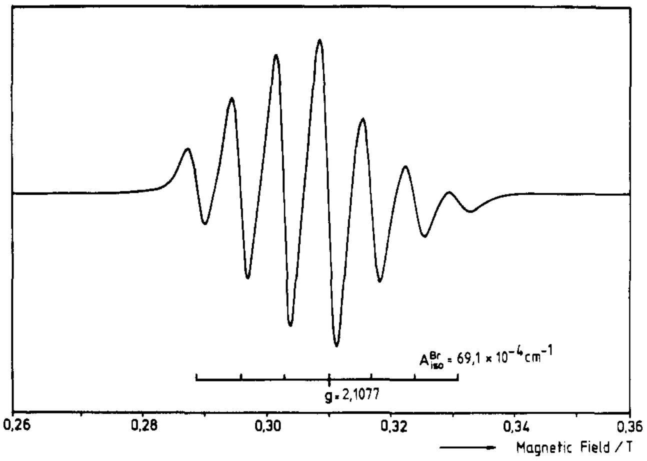

Figure 2. X-Band ESR spectrum of $NiBr_2$(DOHDOpn) in CH_2Cl_2/CCl (1:1) at 310 K (temperature that gives optimum resolution).

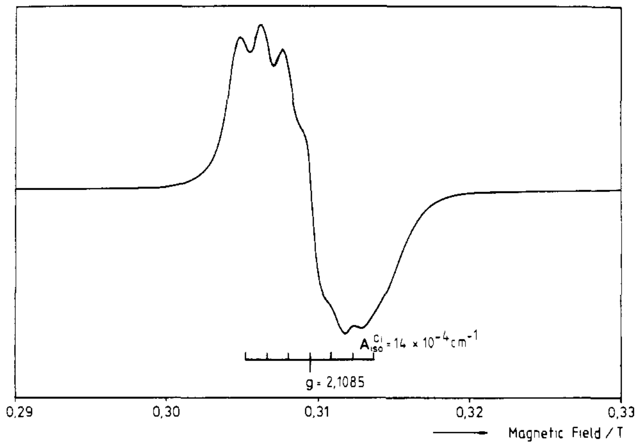

Figure 3. X-Band ESR spectrum of $NiCl_2$(DOHDOpn) in CH_2Cl_2/CCl_4 (1:1) at 250 K (temperature that gives optimum resolution).

The spectra show an almost completely resolved hyperfine structure in the case of the dibromo complex and one which is still clearly discernible in the dichloro complex. By contrast, Co(II) complexes rarely show ESR spectra at room temperature (except with cobyrinic ligands[15]). This is a first indication that the lowest excited states are indeed higher in the Ni(III) complexes compared with the Co(II) complexes. In the latter, it is assumed that relaxation occurs via an *Orbach* mechanism, i.e. a population of a thermally accessible state in which spin–lattice relaxation is very rapid.[16,17]

The g_{iso} values of 2.1099 and 2.1085 (Figures 2 and 3) for the dibromo and the dichloro complexes, respectively, indicate very strongly a metal-centered unpaired electron. The anisotropy of the magnetic parameters can be seen from Figures 4 and 5, which show Q-band spectra of the two complexes in magnetically diluted polycrystalline samples. In both cases halogen hyperfine structure is resolved. In the case of the dibromo complex even all three isotopic species ($^{79}Br^{79}Br$, $^{79}Br^{81}Br$, $^{81}Br^{81}Br$) are clearly seen in the second-derivative trace (Figure 4). Isotopic substitution by ^{61}Ni (90% $I = {}^3/_2$) yields an additional hyperfine splitting that is, however, only discernible in the "parallel" region of the spectrum of the dibromo complex (Figure 6).

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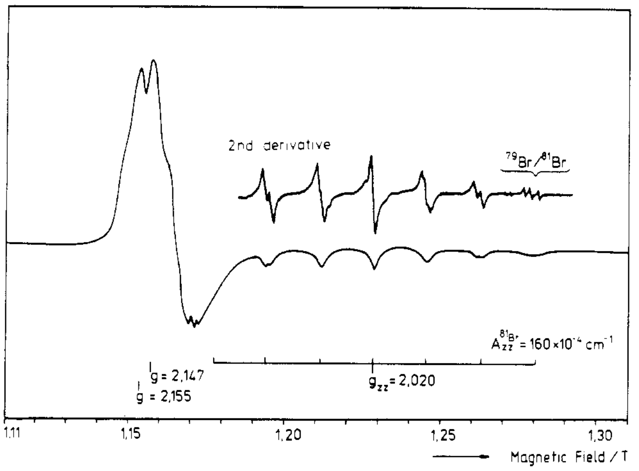

Figure 4. Q-Band ESR spectrum of a powdered sample of $NiBr_2$-(DOHDOpn) as a dopant (1%) in $CoBr_2$(DOHDOpn).

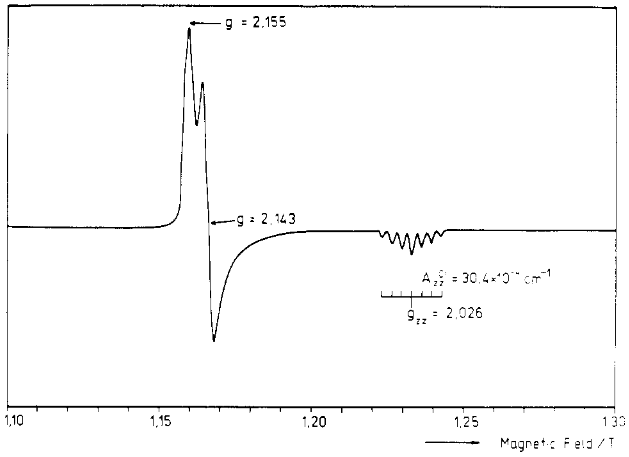

Figure 5. Q-Band ESR spectrum of a powdered sample of $NiCl_2$-(DOHDOpn) as a dopant (1%) in $CoCl_2$(DOHDOpn).

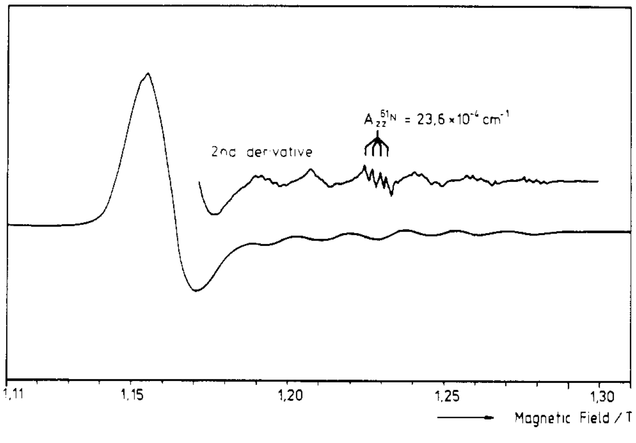

Figure 6. Q-Band ESR spectrum of a powdered sample of $^{61}NiBr_2$(DOHDOpn) as a dopant (0.5%) in $CoBr_2$(DOHDOpn).

Table I. ESR Parameters of $NiBr_2$(DOHDOpn) and $NiCl_2$(DOHDOpn)

ESR parameter	$NiBr_2$-(DOHDOpn)	$NiCl_2$-(DOHDOpn)
g_{zz}	2.020	2.026
g_{xx}	2.155	2.155
g_{yy}	2.147	2.143
g_{iso}	2.108	2.108
$10^4A_{\parallel}(^{81}Br)$, cm^{-1}	160.4	
$10^4A_{\perp}(^{81}Br)$, cm^{-1}	23.4	
$10^4A_{iso}(Br)$, cm^{-1}	69.1	
$10^4A_{zz}(^{61}Ni)$, cm^{-1}	23.6	
$10^4A_{\parallel}(Cl)$, cm^{-1}		30.4
$10^4A_{\perp}(Cl)$,[a] cm^{-1}		5.3
$10^4A_{iso}(Cl)$, cm^{-1}		14.0

[a] $A_{\perp}$ cannot be measured directly from the spectra. It was calculated from A_{iso} and $A_{\parallel}$.

The parameters of both complexes as determined from the frozen- and liquid-solution spectra are given in Table I. Single-crystal ESR spectra of $NiBr_2$(DOHDOpn) and $NiCl_2$(DOHDOpn) doped into the corresponding Co(III) complexes as host lattices yield virtually the same ESR parameter as the frozen-solution spectra. Since the crystal structure of $CoCl_2$(DOHDOpn) has been determined,[18] the principal axes of the **g** and hyperfine tensors could be determined. As expected, the complex has the axis of lowest g value, g_{zz}, perpendicular to the molecular plane determined by the macrocyclic ligand. The values for the spin-Hamiltonian parameters are in good agreement with those determined from the spectra of glassy samples (Table I). The same seems to be true for the dibromo complex, although no definite assignment of the directions can be made, as its crystal structure is unknown. The unit cell contains four magnetically nonequivalent sites, so that the resulting spectra in general orientations of the magnetic field are complicated. Details of the single-crystal measurements are given elsewhere.[19] The hyperfine parameters for the coupling to the halide nuclei are very similar to those found by Raynor et al. in $Ni^{III}X_2$(cyclam)$^+$.[20] The resolution in our single crystal and in the powder spectra is however higher, showing clearly the splitting due to the two isotopes ^{81}Br and ^{79}Br (Figure 4). Consequently, a more precise determination of the coupling parameters is possible. Of the coupling to the ^{61}Ni, only the zz component could be determined. It has almost the same values as that determined by Manoharan et al.[5] in a Ni(III) phosphine complex. It can therefore be assumed that the delocalization of the unpaired electron is of similar importance in all these complexes. Moreover, very little delocalization takes place in the plane of the macrocyclic ligand. In a second-order perturbation calculation,[21] a value $g_{zz} = g_e$ is obtained, if the unpaired electron is in the d_{z^2} orbital. This is in obvious disagreement with the experimentally determined values of g_{zz} = 2.020 and 2.026, which are both significantly larger than the free-electron value. This seems to be a general phenomenon among low-spin Ni(III) complexes.[5] Despite this fact, it cannot be doubted that the unpaired electron is in an orbital with mainly d_{z^2} character, because of the marked halogen hyperfine splitting. If the deviation of g_{zz} from the free-electron value is neglected, approximate energies for the excited doublet states $^2B_2/^2B_1$ of ca. 16900/17500 cm^{-1} for the $NiBr_2$-(DOHDOpn) complex and 16900/18200 cm^{-1} for the $NiCl_2$(DOHDOpn) complex are found.

The general expectation that the energy separation between the ground and first excited doublet states is much larger in Ni(III) complexes than in Co(II) complexes is thus fulfilled. A more detailed interpretation is difficult, however. Even the "refined model",[3] which was used successfully for the interpretation of low-spin Co(II) complexes, does not give a satisfactory explanation of the high g_{zz} values. Other workers[5] who made the same observations included the possibility of

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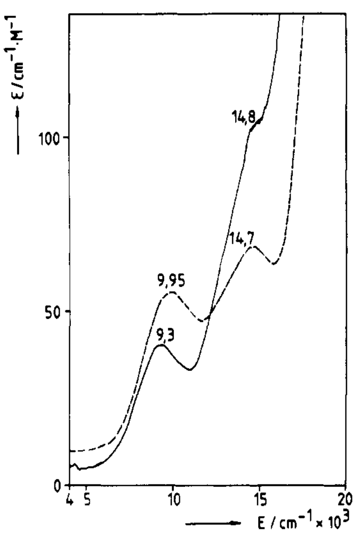

Figure 7. Near-IR/vis spectra of $NiBr_2$(DOHDOpn) (full line) and $NiCl_2$(DOHDOpn) (dashed line) (5×10^{-3} M solutions in dichloromethane; path length 1 cm).

ligand spin-orbit contribution as an explanation. This, however, seems not to be the case in our complexes, since we have only light atoms in the macrocyclic ligand and since the exchange of Cl by Br in the axial position changes g_{zz} only very slightly. A full assignment of the ESR data must therefore include the contribution of quartet states. The present ESR data do not suffice for a complete determination of the numerous parameters needed in such a model. More experimental work, e.g. ENDOR of several nuclei in the complex, is thus necessary.

Electronic Spectra and MO Calculations. Figure 7 gives the electronic spectra of the complexes $NiBr_2$(DOHDOpn) and $NiCl_2$(DOHDOpn) in the near-IR/vis region. In both cases low-energy transitions are present with ϵ of the order of 50 cm^{-1} M^{-1}. Similar transitions were observed in the Ni^{III}-(Me_2cyclam)X_2 complexes[2] and in $Ni(DPG)_2X$. In the case of $NiBr_2$(DOHDOpn) the higher energy band (14800 cm^{-1}) is discernible only as a shoulder on a very intense absorption, which is most probably due to a fully allowed ligand to metal charge-transfer (LMCT) transition. The latter is at a lower energy in $NiBr_2$(DOHDOpn) as compared to that in $NiCl_2$-(DOHDOpn), following the trend generally observed for LMCT transitions.[22]

The low-intensity bands can be attributed to parity-forbidden, spin-allowed d-d transitions. The first excited doublet is therefore at 9300 cm^{-1} in $NiBr_2$(DOHDOpn) and at 10000 cm^{-1} in $NiCl_2$(DOHDOpn). A second transition is found at nearly the same energies (14800 cm^{-1}) in both complexes. These values are much lower than the approximate numbers obtained from the second-order perturbation treatment using the ESR parameters. This discrepancy could be eliminated by using a much more reduced value for the spin-orbit coupling. This is not very meaningful, however, unless more experimental data will be known, which allow for a justifiable choice of parameters in a more complete model.

Semiempirical calculations based on a EHT-SCCC model[19] yield for the orbitals with mainly Ni 3d character the energy scheme represented in Figure 8. The sequence of orbital energies is as expected, and it agrees with the results of ESR spectroscopy as far as the ground state is concerned. d-d transitions are predicted at relatively low energies, but a quantitative agreement between calculated and measured values is not obtained. This is not surprising in view of the approximations inherent in the quantum-chemical model used.

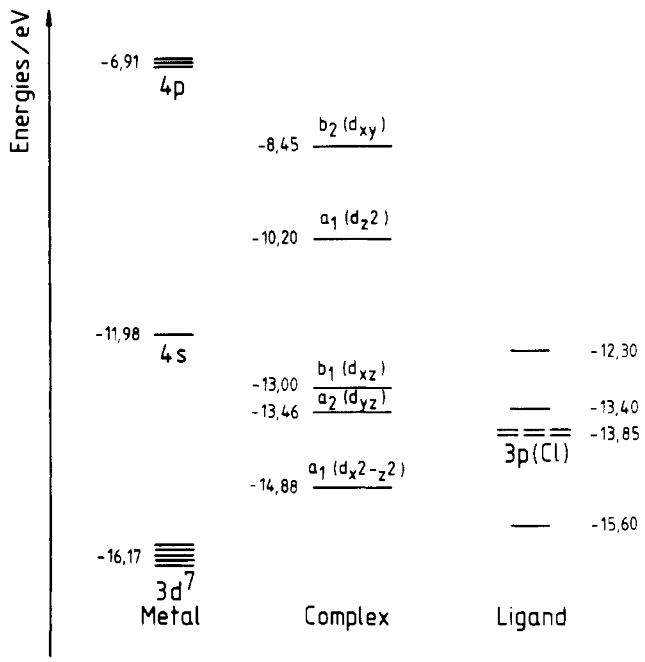

Figure 8. MO diagram of $NiCl_2$(DOHDOpn). Only orbitals with preponderant metal 3d character are displayed.

Kinetic Measurements. Since the two complexes $NiLCl_2$ and $NiLBr_2$ (L = DOHDOpn) show well-resolved ESR spectra in liquid solutions, the halide exchange can be observed easily. Preliminary kinetic measurements indicate a high lability of the Ni-X bond in these complexes. The exchange reaction

$$\mathrm{NiLCl_2 + NiLBr_2 \rightleftarrows 2NiLClBr} \qquad (1)$$

is complete even at -70 °C in CH_2Cl_2/CCl_4 as a solvent,[23] after two 10^{-3} M solutions (ca. 1 min) containing the dichloro and dibromo complexes, respectively, are mixed. The equilibrium concentrations correspond approximately to the statistical ratio.

On the other hand, no exchange takes place between the nickel and the cobalt complexes with the other halide.

$$\begin{gathered}\mathrm{NiLX_2 + CoLY_2 \nrightarrow NiLXY + CoLXY} \\ \mathrm{X, Y = Cl\ or\ Br}\end{gathered} \qquad (2)$$

Solutions containing the nickel and cobalt complexes show no change in their ESR spectra, even after several days at room temperature.

Also, no exchange takes place in solutions containing two kinds of Co complexes.

$$\mathrm{CoLCl_2 + CoLBr_2 \nrightarrow 2CoLClBr} \qquad (3)$$

It is extremely unlikely that the absence of exchange in (2) and (3) is due to a high thermodynamic stability of the "pure" complexes. Rather, an approximate statistical distribution, with preference for the mixed complexes, is to be expected. This is observed indeed in reaction 1. It can be stated, therefore, that the Co(III) complexes show a much higher kinetic stability than the Ni(III) complexes. Since the isostructural complexes of Co(III) and Ni(III) differ just by one electron, a direct comparison can be made.

There are at least two possible mechanistic interpretations for this kinetic behavior:

(1) The exchange reaction between the two nickel complexes proceeds via a bridged transition state/intermediate (Figure

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(23) NiLClBr has an ESR spectrum in fluid solution showing coupling constants of one Cl and one Br, which are, within experimental error, identical, with the ones in the "pure" complexes.

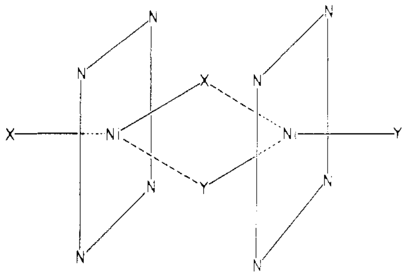

Figure 9. Proposed structure of a bridged transition state/intermediate in the exchange reaction between two nickel complexes.

9), in which the bridging Ni–halide bonds are strongly weakened by the single electron, which occupies essentially the σ-antibonding orbital d_{z^2}. In the Co(III) complexes this orbital is empty and the Co–X bond is therefore much stronger.

(2) The exchange reaction proceeds via a redox step. Two different possibilities exist:

$$2Ni^{III}LBr_2 \rightarrow Ni^{IV}LBr_2^+ + Ni^{II}LBr + Br^- \quad (4)$$

$$Ni^{III}LBr_2 \rightarrow Ni^{II}LBr + {}^1/_2Br_2 \quad (5)$$

In both cases an exchange can take place easily in the five-coordinate Ni(II) species, followed by reoxidation. A purely dissociative substitution reaction is very unlikely in these solvents. More detailed kinetic investigations are in progress.

Acknowledgment. This work was supported by the Swiss National Science Foundation.

Registry No. $NiBr_2$(DOHDOpn), 87306-57-8; $NiCl_2$(DOHDOpn), 87306-58-9; NiI(DOHDOpn), 15137-68-5.

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Complexes of Binucleating Ligands with Two Different Coordination Environments. 4. Electrochemical Properties and Molecular Structure of the Heterobinuclear Complex [5,5′-(1,2-Ethanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)(4–)]nickelcopper, NiCu(BAA)$_2$en

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The electrochemical properties of the heterobinuclear complex [5,5′-(1,2-ethanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)(4–)]nickelcopper, NiCu(BAA)$_2$en, have been investigated with cyclic voltammetry and controlled-potential electrolysis. The CV in dimethylformamide consists of one quasi-reversible wave in the 0- to –2.0-V region with an approximate $E_{1/2}$ of –0.90 V. Addition of an excess of Na^+ as $NaNO_3$ causes a shift of +300 mV and greatly increases the cathodic peak current. The new wave, which is highly reversible in the scan rate range of 0.050–50.000 V/s, is due to two overlapping waves in which the potentials are very similar. The cathodic peak currents in the presence of Na^+ were calculated by using a current function of 0.97, which is consistent with two reversible sequential, one-electron transfers with $E_2° - E_1° = -14$ mV. Agreement between experimental and calculated I_{pc} values was about 2% over the entire scan rate range on this basis when a small amount of weak reactant adsorption was included. The electrochemical properties of the binuclear complex were compared to those of related mononuclear Ni(II) and Cu(II) complexes in order to assess the significance of the presence of the two metal centers. As a means of understanding the electrochemistry in the context of structural properties, NiCu(BAA)$_2$en ($C_{26}H_{24}N_2O_4CuNi$) was crystallized from the electrochemical solvent, DMF, and examined by X-ray techniques. The structure consists of dimers of heterobinuclear molecules in which the copper is bound to four ketonic oxygens and the nickel is bound to two ketonic oxygens and two nitrogens from the ethylenediamine moiety. The intramolecular Ni–Cu distance is 2.925 Å. The distance between the mean planes of the molecules in the dimer is 3.21 Å. One of the methine carbons of the ligand backbone of one molecule lies 3.06 Å above the copper atom of the second molecule. The copper is displaced 0.11 Å out of the molecular plane toward this carbon in a typical square-pyramidal fashion. Crystal data: $P2_1/c$, $a = 13.052$ (2) Å, $b = 8.612$ (2) Å, $c = 20.295$ (4) Å, $\beta = 98.38$ (2)°, $Z = 4$, $R_1 = 0.050$, $R_2 = 0.051$.

Introduction

In previous papers in this series we have described a systematic synthetic approach to the preparation of heterobinuclear complexes based upon the selectivity of the different coordination sites in the Schiff-base diamine derivatives of 1,3,5-triketonates.[1] In several instances, it has been possible to isolate and characterize both the mononuclear precursors and the heterobinuclear complexes that result from binding the two metal ions to the same ligand molecule.[1a,2] With this approach and, by comparison to the mononuclear precursors, it is possible to deterimine the effect of two metal ions per molecule on the chemical and physical properties.

The electrochemical properties of polynuclear transition-metal complexes have been of primary interest to use as a means of determining the chemical significance of having two or more metal ions per molecule that are close enough to have some reasonable interaction. Previously, we have described the unusual electrochemistry associated with the binuclear Cu(II) complexes of 1,3,5-triketonates and their diamine Schiff bases.[3-5] The results of these electrochemical studies in the presence of excess Na^+ are consistent with two reversible, sequential, one-electron transfers at the same (or very nearly the same) potential. This interpretation is based upon the

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