electron exchange,[1] the splittings caused by magnetic dipole interactions where the electron exchange between the coupled metal ions is relatively slow also have the potential to provide quite accurate estimates of the metal–metal separation.

Interpretation of the *g* Values of the Complex. For a complex of rhombic symmetry such as $CuCl_2(H_2O)_2$, to a first approximation the molecular *g* values are related to the excited-state energies E_{xz}, E_{yz}, and E_{xy} by the expressions[11]

$$g_x = 2.002 - 2\lambda k_{\perp}^2(a - 3^{1/2}b)^2/E_{yz} \quad (2a)$$

$$g_y = 2.002 - 2\lambda k_{\perp}^2(a + 3^{1/2}b)^2/E_{xz} \quad (2b)$$

$$g_z = 2.002 - 8\lambda k_{\parallel}^2 a^2/E_{xy} \quad (2c)$$

The constants *a* and *b* in these equations define the proportions of the $d_{x^2-y^2}$ and d_{z^2} orbitals in the ground-state wave function, which is of the form $ad_{x^2-y^2} - bd_{z^2}$. Substitution into eq 2a–c of $\lambda = -828$ cm^{-1}, together with the observed molecular values $g_x = 2.049$, $g_y = 2.081$, and $g_z = 2.269$ and excited-state energies $E_{xy} = 13\,400$ cm^{-1}, $E_{xz} = 14\,500$ cm^{-1}, and $E_{yz} = 14\,600$ cm^{-1} obtained from the electronic spectrum of the complex,[15] yields the orbital reduction parameters $k_{\parallel}^2 = 0.54$ and $k_{\perp}^2 = 0.55$ and a value $b = 0.074$ for the mixing coefficient of the d_{z^2} orbital in the ground-state wave function. As expected, the orbital reduction parameters lie approximately midway between the values of ~0.65 and ~0.4 observed for the $Cu(H_2O)_6^{2+}$ [11] and $CuCl_4^{2-}$ ions,[8] respectively. It should be noted that this approach considers that the in-plane *g* anisotropy is dominated by the difference in the metal–ligand perturbation along the *x* and *y* axes. In effect, this assumes that any differences in the contributions from the ligand parts of the ground-state wave functions are insignificant. In the case of the axially symmetric planar $CuCl_4^{2-}$ ion calculations suggest that the net contribution to the *g* shift due to the orbital angular momentum associated with the ligand part of the ground-state wave function is quite small,[16] but this is largely because of the cancellation of significant terms derived by including charge-transfer excited states and ligand spin–orbit coupling effects. It must be stressed that it is not clear to what extent the different covalencies of the Cu–O and Cu–Cl bonds will affect the *g* anisotropy in a mixed-ligand complex such as $CuCl_2(H_2O)_2$, so that the present interpretation must be viewed with caution.

Simple theory suggests that *b* should be related to the difference in the σ perturbation produced by the ligands along the *x* and *y* axes. It is known that H_2O lies slightly higher in the spectrochemical series than Cl^- when bonded to a first-row transition-metal ion, but measurements made on octahedral complexes cannot distinguish between the contributions made by σ and π bonding to the overall ligand field splitting.[17] The fact that *b* is positive in $CuCl_2(H_2O)_2$, with g_x being parallel to the $Cu-OH_2$ bond directions, suggests that water is a stronger σ donor than chloride toward copper(II).[18] The angular-overlap model provides a useful way of quantifying metal–ligand interactions, and this suggests[19] that in a planar complex such as *trans*-$CuCl_2(H_2O)_2$

$$b \approx \tfrac{1}{2}(3^{1/2})(e_{\sigma x} - e_{\sigma y})/(e_{\sigma x} + e_{\sigma y}) \quad (3)$$

Here, $e_{\sigma x}$ and $e_{\sigma y}$ represent the σ-antibonding perturbations due to one water and one chloride ligand, respectively. These perturbations are related to the diatomic overlap integrals S_σ between the metal d and ligand p orbitals by the expression $e_\sigma = KS_\sigma^2$, where *K* is a constant.[11] Studies of the electronic spectra of a range of chlorocuprate(II)[8] and hexaaquocuprate(II)[11] complexes suggest that $K_\sigma(H_2O) \simeq 8.6 \times 10^5$ cm^{-1} and $K_\sigma(Cl^-) \simeq 9.4 \times 10^5$ cm^{-1}, and these values, together with the diatomic overlap integrals[20] $S_\sigma = 0.094$ and $S_\sigma = 0.083$ appropriate to the bond distances Cu–O = 1.90 Å and Cu–Cl = 2.23 Å in $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$,[10] yield the parameters $e_{\sigma x} = 7600$ cm^{-1} and $e_{\sigma y} = 6475$ cm^{-1}. Substitution of these values into eq 3 suggests a mixing coefficient $b = 0.069$ in good agreement with the value $b = 0.074$ obtained from the EPR parameters. While it must be emphasized that the agreement may be purely fortuitous, the self-consistency of the results is gratifying and suggests that the angular-overlap model holds considerable promise as a means of parametrizing the metal–ligand interactions in low-symmetry metal complexes, such as those that are often present in molecules of biological importance.

Acknowledgment. The financial assistance of the Australian Research Grants Commission is gratefully acknowledged, and the Central Science Laboratory of the University of Tasmania is thanked for providing the facilities for the EPR measurements.

Registry No. $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$, 72268-10-1.

Supplementary Material Available: A listing of the crystal *g* values for $[CuCl_2(H_2O)_2][(C_6H_5)_3PO]_4$ (1 page). Ordering information is given on any current masthead page.

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(16) Smith, D. W. *J. Chem. Soc. A* **1970**, 3108. Cassidy, P. Hitchman, M. A. *Inorg. Chem.* **1977**, *16*, 1568.

(17) See, for example: Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968.

(18) Hitchman, M. A.; Olsen, C. D.; Belford, R. L. *J. Chem. Phys.* **1969**, *50*, 1195. Hitchman, M. A. *J. Chem. Soc. A* **1970**, 4.

(19) See ref 11 for the angular-overlap matrix elements; eq 3 results from the application of simple perturbation theory—see ref 12, p 245.

(20) Smith, D. W. *J. Chem. Soc. A* **1970**, 498.

Contribution from the Chemistry Departments,
Ben-Gurion University of the Negev
and Nuclear Research Centre Negev, Beer-Sheva, Israel

Ligand–Metal Interrelationships. 2. Effect of the Change from Square-Planar to Octahedral Coordination on the pK_a of the Ligand in Unsaturated Tetraaza Macrocyclic Nickel Complexes: A Pulse-Radiolytic Study

Haim Cohen,* Mordechi Nutkovich,* Dan Meyerstein,*
and Alan Shusterman*

Received November 18, 1983

We have recently reported that the pK_a of the macrocylic ligand in the tervalent nickel complex of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene, NiL_1^{3+}, is higher than the pK_a measured for the divalent complex, NiL_1^{2+}.[1] This surprising result, in view of the greater acidity expected for the tervalent nickel complex, was explained by the observation that the pK_a predicted for the ligand in this complex coincides with the pH range in which two hydroxyl groups are axially coordinated to the nickel. Thus, the results only indicate that $Ni(OH)_2^+$ has a smaller effect on the ligand pK_a than does Ni^{2+}. In addition, we had tentatively assigned the strong absorption, $\lambda_{max} = 600$ nm, observed for the alkaline form of the tervalent complex as a ligand-to-metal charge-transfer transition.[1]

In order to confirm these conclusions we examined the nickel complex of 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,13-diene, NiL_2^{3+}. It was observed that the trifluoromethyl group sufficiently stabilizes the alkaline form

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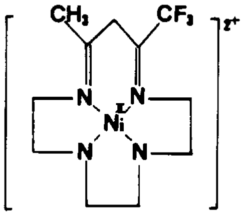
*Addresses for correspondence: M.N., D.M., and A.S., Ben-Gurion University of the Negev; H.C., Nuclear Research Centre Negev.

of L_2 not only to cause a blue shift in the charge-transfer transition of the tervalent complex but also to lower the pK_a of the ligand to a pH range where aquo groups and not hydroxyl groups are coordinated to the tervalent nickel. Even so, it was discovered that the pK_a of NiL_2^{3+} was still greater than that of NiL_2^{2+}. We suggest that this ordering is caused by changes in the energy of the unfilled axial $4p_z$ orbital of the nickel, which is destablized in the 6-coordinate tervalent complex relative to the 4-coordinate divalent complex.



NiL_2^{2+}

The complex $Ni(L_2\text{-}H)^+ClO_4^-$ was synthesized by the literature method.[2,3] The pK_a of NiL_2^{2+} was found to be 0.84 ± 0.15 by measuring the change in absorbance of the $Ni(L_2\text{-}H)^+$ absorption band at 368.5 nm ($\epsilon_{max} = 5700$ M^{-1} cm^{-1}).[4] $Ni(L_2\text{-}H)^+$ was also oxidized by $Br_2^-\cdot$ radicals in the pH range 3–12.[5] The spectral changes observed are consistent with the reactions (1)–(4).

$$Ni(L_2\text{-}H)^+ + Br_2^-\cdot + 2H_2O \rightarrow NiL_2(H_2O)Br^{2+} + OH^- + Br^- \qquad k = 5.0 \times 10^9\ M^{-1} \tag{1}$$

$$NiL_2(H_2O)Br^{2+} \xrightarrow{\text{base}} Ni(L_2\text{-}H)(H_2O)_2^{2+} + Br^- \tag{2}$$

$$Ni(L_2\text{-}H)(H_2O)_2^{2+} + H_3O^+ \rightleftarrows NiL_2(H_2O)_2^{3+} \qquad pK_a = 5.1 \pm 0.3 \tag{3}$$

$$2Ni(L_2\text{-}H)(H_2O)_2^{2+} \rightarrow \text{dimer} \qquad 2k = 1.5 \times 10^8\ M^{-1}\ s^{-1} \tag{4}$$

Reaction 1 was monitored by measuring the rate of disapperance of $Br_2^-\cdot$ radicals at 380 nm and also by measuring the rate of formation of $Ni(L_2\text{-}H)(H_2O)_2^{2+}$[7] at 580 nm in the cases where the pH was greater than 9.0, since reaction 2 is faster than reaction 1 under these conditions. In the pH range 4–7, the rate of disappearance of $Br_2^-\cdot$ is unchanged but the rate of formation of $Ni(L_2\text{-}H)(H_2O)_2^{2+}$ at 580 nm is slow.

We attribute this formation to reaction 2 ($k = 1.0 \times 10^3$ and 7.6×10^4 s^{-1} at pH 4.8 and 8.4, respectively), a reaction that was not observed for $NiL_1(H_2O)_2^{3+}$ but has been reported for other nickel tetraazamacrocycle complexes.[6,8,9] The spectrum of $Ni(L_2\text{-}H)(H_2O)_2^{2+}$ [$\lambda^1_{max} = 355$ nm ($\epsilon_{max} = 4600$ M^{-1} cm^{-1}), $\lambda^2_{max} = 580$ nm ($\epsilon_{max} = 1800$ M^{-1} cm^{-1})] is similar to that of $Ni(L_1\text{-}H)(H_2O)_2^{2+}$ [$\lambda^1_{max} = 330$ nm ($\epsilon_{max} = 6850$ M^{-1} cm^{-1}), $\lambda^2_{max} = 600$ nm ($\epsilon_{max} = 2500$ M^{-1} cm^{-1})].[1] The blue shift of λ^2_{max} when a CH_3 substituent is replaced by a CF_3 substituent is consistent with our earlier assignment of this absorption to a ligand-to-metal charge-transfer transition. This assignment was based on the high intensity of the absorption band and on the expected relative redox potentials of the central tervalent nickel and its ionic ligand. The parallel red shift of λ^1_{max} and the fact that this band is only slightly higher in energy than a similar band of $Ni(L_2\text{-}H)^+$ suggest that this absorption is a ligand-centered $\pi \rightarrow \pi^*$ transition.

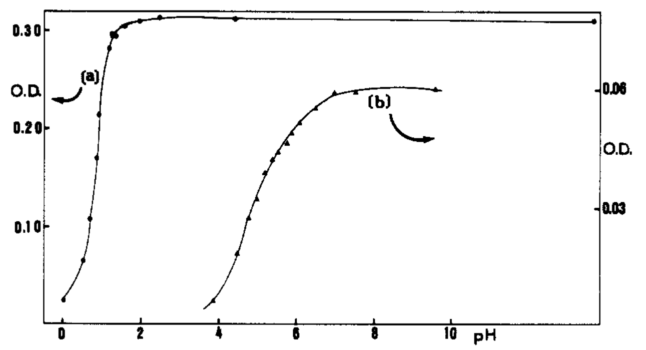


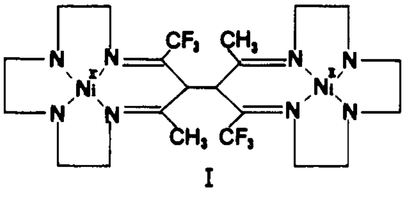
Figure 1. Determination of the pK_a's: (a) NiL_2^{2+}, measured at 368.5 nm; (b) $NiL_2(H_2O)_2^{3+}$, measured at 580 nm.

Table I. pK_a of the Ligand in NiL_1 and NiL_2 Complexes

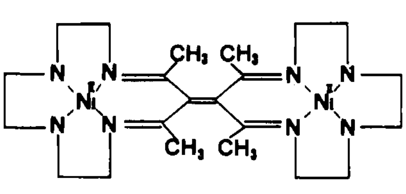
	L_1	L_2
NiL_i^{2+}	6.55	0.84
$NiL_i(H_2O)_2^{3+}$	8.8	5.1

The fact that no low-energy LMCT absorption is observed prior to the loss of bromide in reaction 2 suggests that the pK_a of $NiL_2(H_2O)Br^{2+}$ is considerably higher than that of $NiL_2(H_2O)_2^{3+}$ or $NiL_2(OH)_2^+$, whichever of the two is present in the pH range 4–6. This observation is in agreement with similar observations for analogous Co(III) complexes.[10]

The complex $Ni(L_2\text{-}H)(H_2O)_2^{2+}$ decomposes in a second-order reaction, $2k = 1.5 \times 10^8$ M^{-1} s^{-1}. The product of this reaction was not identified, but we believe it is dimer I (or one of its alkaline forms) since the oxidation of $Ni(L_1\text{-}H)^+$ by $S_2O_8^{2-}$ and I_2 has been shown to yield dimer II.[11,12]



I



II

The pK_a of $NiL_2(H_2O)_2^{3+}$ was determined by measuring the pH effect on the intensity of the absorption at 580 nm and

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(1) Ulman, A.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta Lett.* **1982**, *64*, L127.

(2) Cummings, S. C.; Sievers, R. E. *Inorg. Chem.* **1970**, *9*, 1131.

(3) The purity of $Ni(L_2\text{-}H)NO_3$ was checked by NMR, IR, and UV-vis spectrophotometry. The results were identical within the experimental error limit to those reported by Cummings and Sievers.[2] The perchlorate complex was prepared by exchanging the nitrate with perchlorate.

(4) The large error limit is probably due the fact that the ionic strength changes considerably in the region 0 < pH < 1 and that no effort to correct for activity was made.

(5) The experimental technique and the conditions used were identical with those earlier described.[1,6] Solutions in the pH range 4.0–10.0 were buffered with 1×10^{-3} M acetate or phosphate.

(6) Jaacobi, M.; Meyerstein, D.; Lilie, J. *Inorg. Chem.* **1979**, *18*, 429.

(7) Or $Ni(L_2\text{-}H)(OH)_2$ or $Ni(L_2\text{-}H)(OH)H_2O^+$, as appropriate at each pH. The pK_a of the axially bound aquo ligands is not known and seems to have no effect on the results. Therefore, $Ni(L_2\text{-}H)(H_2O)_2^{2+}$ is used representing all three forms.

(8) (a) Ferraudi, G.; Muralidharan, S. *Inorg. Chem.* **1981**, *20*, 4262. (b) Maruthmuthu, P.; Patterson, L. K.; Ferraudi, G. *Ibid.* **1978**, *17*, 3157. (c) Morliere, P.; Patterson, L. K.; Ibid. **1981**, *20*, 1458. (d) Morliere, P.; Patterson, L. K. *Ibid.* **1982**, *21*, 1837.

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(10) Suitzer, J. A.; Endicott, J. F.; Khalifa, M.; Rotzinger, F. P.; Kumar, K. *J. Am. Chem. Soc.* **1983**, *105*, 56.

(11) Nutkovich, M.; Meyerstein, D., unpublished results.

(12) Cunningham, J. A.; Sievers, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 7183.

was found to be 5.1 ± 0.3[13] (Figure 1). This value is much higher than that of the divalent complex NiL_2^{2+} (Table I). Since the pK_a of NiL_2^{2+}, 0.84, is much lower than that of the aquo ligands of $NiL_2(H_2O)_2^{3+}$, the high pK_a of the latter complex cannot be a consequence of the prior deprotonation of the aquo ligands as we had previously proposed for $NiL_1(H_2O)_2^{3+}$.[1] Clearly, the oxidation state of the metal atom, even when the presence of other ligands is accounted for, is not the factor controlling the pK_a of the macrocylic ligand. Rather, the low pK_a's found for the divalent complexes, NiL_1^{2+} and NiL_2^{2+}, appear to be the result of a special stabilization of the deprotonated ligands that does not occur in the 6-coordinate tervalent complexes. A possible source of this stabilization might be the favorable interaction of the unfilled $4p_z$ orbital of the nickel with the HOMO of the π system of the deprotonated ligand. This interaction will be greatest when the $4p_z$ is low in energy, which is the case for the square-planar divalent complexes where the $4p_z$ is nonbonding. On the other hand, in the tervalent complexes, only a small π(HOMO)–$4p_z$ interaction is possible since the $4p_z$ orbital is antibonding as a result of its interaction with the axial ligands. Thus, the results suggest that due to the change in the coordination number the energy of the $4p_z$ orbital is raised when the nickel is oxidized though the opposite effect occurs in the noncoordinated cation.

These conclusions are in accord with the observation that the pK_a's of analogous tervalent cobalt complexes are in the range 5–8,[10] i.e. in the same range observed for tervalent nickel complexes, suggesting that the pK_a's of the divalent nickel complexes are the "abnormal" values. Also consistent with this explanation is the observation that the pK_a's of 13- and 14-membered macrocyclic divalent nickel complexes are 2–3 pK units lower than those of the analogous divalent copper complexes.[15] The high pK_a's of the latter probably stem from the fact that the copper is 6- or 5-coordinate, though Jahn-Teller distorted, and not from the difference in the radii of divalent nickel and copper as has been suggested.[15]

Acknowledgment. This study was supported in part by the Israel-U.S. Binational Science Foundation (BSF), Jerusalem, Israel, and by PEF, Israel Endowment Funds, Inc., New York.

Registry No. L_2, 90367-70-7; NiL_2^{2+}, 90367-68-3; $NiL_2(H_2O)_2^{3+}$, 90367-69-4; Br_2^-, 12595-70-9.

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[13] The relatively high error limit seems to stem from the fact that the pK_a of the aquo ligands occurs in the same pH range[6,13] and therefore the slope of the plot in Figure 1 is somewhat smaller than theoretically predicted.

[14] Zeigerson, E.; Ginzburg, G.; Beker, J.; Kirschenbaum, L. J.; Cohen, H.; Meyerestein, D. *Inorg. Chem.* **1981**, *20*, 3988.

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Contribution No. 6963 from the Department of Chemistry,
California Institute of Technology, Pasadena, California 91125

Crystal Structure of the Cis,cis,trans Isomer of $PtCl_2(NH_3)_2(OH)_2$: Corrigendum

Richard E. Marsh

Received December 20, 1983

Recently, the crystal structures of three isomers of $PtCl_2(NH_3)_2(OH)_2$ were reported.[1] The structure of the cis,cis,trans isomer was described as tetragonal, space group $P4_2/n$. It should properly be described in space group $P4_2/nmc$.

The coordinates given in Table III of ref 2 correspond to the symmetry of $P4_2/nmc$ within their reported esd's, the Cl and N atoms lying on a mirror plane at $y = {}^3/_4$ and the O atom on a mirror plane at $x = {}^1/_4$; the anisotropic coefficients U_{ij} (obtained as supplementary material) also show the additional symmetry within their esd's. The c-glide plane of $P4_2/nmc$ requires the systematic absence of reflections hhl with l odd; none of these reflections appear in the supplementary table, a list of 599 reflections with, presumably, $I \geq 2.0\sigma(I)$. The higher Laue symmetry ($4/mmm$ rather than $4/m$) is readily apparent from both the F_o and F_c values in this table.

Curiously, the same mistake in space group assignment was also made by earlier investigators.[2]

Registry No. $PtCl_2(NH_3)_2(OH)_2$, 31246-66-9.

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[1] Kuroda, R.; Neidle, S.; Ismail, I. M.; Sadler, P. J. *Inorg. Chem.* **1983**, *22*, 3620.

[2] Faggiani, R.; Howard-Lock, H. E.; Lock, C. J. L.; Lippert, B.; Rosenberg, B. *Can. J. Chem.* **1982**, *60*, 529.

Contribution from Chemistry Department I,
Inorganic Chemistry, H. C. Ørsted Institute,
University of Copenhagen, DK-2100 Copenhagen Ø, Denmark,
and Department of Chemistry, The University of
North Carolina, Chapel Hill, North Carolina 27514

Structural and Magnetic Characterization of the Triclinic Modification of Bis(μ-hydroxo)bis[tetraamminechromium(III)] Chloride Tetrahydrate, $[(NH_3)_4Cr(OH)]_2Cl_4\cdot4H_2O$

Derek J. Hodgson*[1a] and Erik Pedersen[1b]

Received November 2, 1983

In recent years there have been numerous studies of the structural and magnetic properties of bis(μ-hydroxo)chromium(III) complexes[2–13] and their alkoxo-bridged analogues.[14] A principal aim of this work has been the establishment of a correlation between the isotropic ground-state exchange coupling parameter (J) and the structure of the dimeric unit. While initial attention was focused on the influence of the bridging Cr–O–Cr angle (ϕ), in analogy with the result found in copper(II) systems,[15] more recent work has noted the major significance of the dihedral angle (θ) between the bridge plane and the O–H vector.[5,6,11–14,16–18] Unfortunately, since hydrogen

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[1] (a) The University of North Carolina. (b) H. C. Ørsted Institute, University of Copenhagen.

[2] Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1980**, *19*, 3116.

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