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.

---

(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.

(15) Martin, J. G.; Cummings, S. *Inorg. Chem.* **1973**, *12*, 1477.

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.

---

(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, $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$

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

---

(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.

(3) Cline, S. J.; Glerup, J.; Hodgson, D. J.; Jensen, G. S.; Pedersen, E. *Inorg. Chem.* **1981**, *20*, 2229.

(4) Scaringe, R. P.; Hodgson, D. J.; Hatfield, W. E. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 340.

(5) Cline, S. J.; Hodgson, D. J.; Kallesøe, S.; Larsen, S.; Pedersen, E. *Inorg. Chem.* **1983**, *22*, 637.

(6) Glerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 161.

(7) Srdanov, G.; Herak, R.; Radanovic, D. J.; Veselinovic, D. S. *Inorg. Chim. Acta* **1980**, *38*, 37.

(8) Larsen, S.; Hansen, B. *Acta Chem. Scand., Ser. A* **1981**, *35*, 105.

(9) Oki, H.; Yoneda, H. *Inorg. Chem.* **1981**, *20*, 3875.

(10) Hatfield, W. R.; MacDougall, J. J.; Shepherd, R. E. *Inorg. Chem.* **1981**, *20*, 4216.

(11) Decurtins, S.; Güdel, H. U.; Pfeuti, A. *Inorg. Chem.* **1982**, *21*, 1101.

(12) Decurtins, S.; Güdel, H. U. *Inorg. Chem.* **1982**, *21*, 3598.

(13) Kallesøe, S.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 859.

(14) Fischer, H. R.; Glerup, J.; Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1982**, *21*, 3063 and references therein.

(15) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173 and references therein.

0020-1669/84/1323-2363$01.50/0