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.

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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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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]

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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.

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Table I. Crystallographic and Data Collection Parameters

$a = 6.727\ (3)$ Å
$b = 7.859\ (2)$ Å
$c = 10.286\ (7)$ Å
$\alpha = 92.42\ (4)^\circ$
$\beta = 106.77\ (4)^\circ$
$\gamma = 106.15\ (3)^\circ$

$V = 495.6\ (9)$ Å^3
$Z = 1$
space group: $P\bar{1}$
NO = 1998 $[I > 3\sigma(I)]$
$\mu = 16.42$ cm^{-1}
data range: $2^\circ < 2\theta(\mathrm{Mo}) < 55^\circ$

atom coordinates in relatively large structures are usually imprecisely known, the angle θ is rarely determined accurately in X-ray structural studies.

Our successful crystallization[5] of two salts of the simple cation bis(μ-hydroxo)bis[tetraamminechromium(III)], $[(NH_3)_4Cr(OH)]_2^{4+}$, provided us with a system in which θ could be precisely determined by virtue of the small number of crystallographic parameters. We noted with some interest that the chloride salt was not isomorphous with the known cobalt(III) analogue, but was monoclinic[5] rather than triclinic.[19,20] Shortly after we performed those experiments, we learned that Güdel and co-workers had isolated a different form of this complex (and of its bromide analogue), which is isomorphous with the cobalt complex.[11,12] Moreover, the magnetic properties of this triclinic form were demonstrated by Güdel and co-workers[12] to be markedly different from those we had reported for the monoclinic form.[5] Regrettably, while the gross structural features of the cobalt(III) complex were reported more than 20 years ago by two independent workers,[19,20] no detailed structural information concerning the bridging moiety for either the cobalt or the chromium complex was available. Consequently, we have now determined the structure of the triclinic modification of the chromium complex, triclinic $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$, and have examined the temperature dependence of its magnetic susceptibility.

Experimental Section

Preparation of the Complex. The complex $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$ was prepared as described earlier.[5,11] Crystals of the triclinic form were originally obtained by seeding a concentrated aqueous solution at 0 °C (in the dark) with a few crystals of the cobalt analogue. Subsequently, crystals from these early preparations were used as seed crystals, and eventually we found that the triclinic form crystallized spontaneously in preference to the monoclinic form from some preparations. The triclinic form is significantly less soluble than the monoclinic form.

Magnetic Susceptibility Measurements. The magnetic susceptibility of microcrystalline samples of the complex was measured by the Faraday method at a field strength of 12 000 Oe in the temperature range 2.38–240 K. Descriptions of the instrumentation and data analysis techniques are available elsewhere.[16,17]

Crystallographic Measurement. A red, prismatic crystal of the complex was mounted on an Enraf-Nonius CAD-4 diffractometer; preliminary analysis demonstrated that the complex belongs to the triclinic system, the cell chosen being consistent with the space groups $P\bar{1}$ and $P1$. The data collection parameters and cell constants are listed in Table I. The cell constants obtained here for the chromium complex are very similar to those reported for the cobalt analogue, the volume of 495.6 (9) Å^3 here being 5% larger than that of 469.2 Å^3 reported by Prout.[19]

Solution and Refinement of the Structure. The assumed isomorphism with the cobalt analogue was checked by examination of a Patterson function. Isotropic least-squares refinement of the 10 heavy atoms using the corresponding parameters from the cobalt structure as determined by Prout[19] gave values of the conventional agreeement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and R_2 (weighted R factor) $= [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ of 0.078 and 0.082, respectively. In all least-squares calculations, refinement was carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were assigned as $4F_o^2/\sigma^2(F_o)^2$, where $(F_o)^2$ is given by $[\sigma^2(I) + (0.02)^2I^2]^{1/2}$ and $\sigma^2(I)$ is derived from counting statistics alone. Anisotropic refinement reduced the values of R_1 and R_2 to 0.050 and 0.064, respectively, and examination of a subsequent difference Fourier map revealed the location of all 17 hydrogen atoms. The final least-squares calculation, which involved anisotropic refinement of all non-hydrogen atoms and isotropic refinement of hydrogen atoms, gave values of R_1 and R_2 of 0.024 and 0.033, respectively; no parameter experienced a shift of more than 0.4σ, which was taken as evidence of convergence. A final difference Fourier was featureless, with no peak higher than 0.12 e Å^{-3}. All computer programs used were those provided by Enraf-Nonius in the CAD-4/SDP package.

The refined non-hydrogen atomic positional parameters, along with their estimated standard deviations, are collected in Table II. The hydrogen atom coordinates, anisotropic librational parameters, and a listing of observed and calculated structure amplitudes are available as supplementary material.

Table II. Positional Parameters in $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$

atom	x	y	z
Cr	0.01287 (3)	0.00902 (2)	0.15028 (2)
Cl1	0.35519 (5)	0.66596 (4)	0.05480 (4)
Cl2	0.15988 (6)	0.31293 (5)	0.53799 (4)
O1	0.1990 (1)	0.0119 (1)	0.03252 (9)
O2	0.3909 (2)	0.6803 (2)	0.74955 (12)
O3	0.3232 (2)	0.6868 (2)	0.39934 (14)
N1	0.0950 (2)	0.2854 (2)	0.1809 (1)
N2	−0.0699 (2)	−0.2651 (2)	0.1484 (1)
N3	0.2642 (2)	0.0332 (2)	0.3293 (1)
N4	−0.2147 (2)	0.0014 (2)	0.2524 (1)

Table III. Bond Distances (Å) in $[(NH_3)_4Cr(OH)]_2^{4+}$

atoms	dithionate[a]	monoclinic chloride[a]	triclinic chloride[b]
Cr–Cr	3.045 (1)	3.023 (1)	3.041 (1)
Cr–O1	1.968 (1)	1.980 (1)	1.974 (1)
Cr–O1′	1.962 (2)	1.969 (1)	1.972 (1)
Cr–N1	2.082 (2)	2.084 (1)	2.073 (1)
Cr–N2	2.081 (2)	2.083 (2)	2.068 (1)
Cr–N3	2.078 (2)	2.074 (1)	2.068 (1)
Cr–N4	2.081 (2)	2.089 (1)	2.081 (1)
O1–H1	0.73 (2)	0.80 (2)	0.73 (1)

[a] Data are from ref 5, but atoms have been renumbered to be consistent with the numbering scheme in Figure 1, i.e. in all cases N4 is trans to O1 etc. [b] This work.

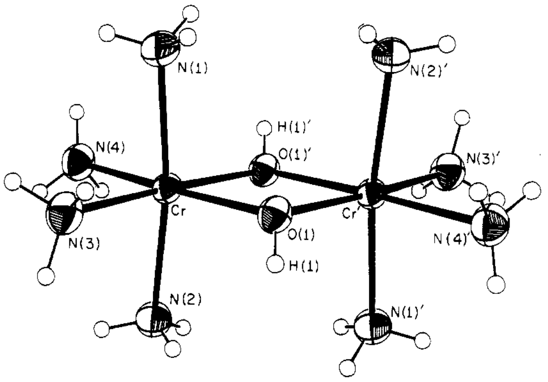

Figure 1. View of the $[(NH_3)_4Cr(OH)]_2^{4+}$ cation in the triclinic form of $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$. Thermal parameters are drawn at the 50% probability level, but hydrogen atoms are shown as spheres of arbitrary size.

Results and Discussion

The structure consists of dimeric $[(NH_3)_4Cr(OH)]_2^{4+}$ cations that are linked by hydrogen bonds to anions and solvent molecules. The geometry of one dimer is shown in Figure 1. The principal bond lengths and angles are compared in Tables III and IV with the values reported earlier[5] for the other crystal forms of this cation. The geometry at the chromium(III) centers is roughly octahedral, the ligating atoms being the two

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Table IV. Bond Angles (deg) in the $[(NH_3)_4Cr(OH)]_2{}^{4+}$ Cation

atoms	dithionate[a]	monoclinic chloride[a]	triclinic chloride[b]
Cr-O1-Cr′	101.54 (5)	99.92 (3)	100.83 (3)
O1-Cr-O1′	78.46 (4)	80.08 (3)	79.17 (3)
O1-Cr-N1	91.84 (5)	92.67 (3)	92.94 (4)
O1-Cr-N2	95.39 (6)	93.39 (3)	93.76 (4)
O1-Cr-N3	91.98 (5)	91.40 (3)	93.55 (4)
O1-Cr-N4	172.86 (9)	176.2 (3)	172.99 (3)
O1′-Cr-N1	94.17 (6)	93.25 (3)	93.46 (4)
O1′-Cr-N2	90.72 (5)	90.29 (3)	92.48 (4)
O1′-Cr-N3	170.1 (1)	171.44 (6)	172.72 (4)
O1′-Cr-N4	94.61 (5)	96.10 (3)	93.83 (4)
N1-Cr-N2	171.96 (7)	173.44 (7)	171.77 (4)
N1-Cr-N3	88.55 (6)	87.95 (3)	86.55 (4)
N1-Cr-N4	86.87 (6)	87.43 (3)	87.81 (4)
N2-Cr-N3	87.70 (6)	89.37 (4)	88.27 (4)
N2-Cr-N4	86.37 (6)	86.70 (3)	86.11 (4)
N3-Cr-N4	95.01 (5)	92.42 (3)	93.45 (4)
Cr-O1-H1	123 (2)	118 (2)	114 (1)
Cr′-O1-H1	127 (2)	120 (2)	114 (1)

[a] See footnote to Table III; data from ref 5. [b] This work.

oxygen atoms of the hydrogen bridges and four ammonia nitrogen atoms. The Cr-N distances are in the range 2.068 (1)-2.081 (1) Å, which is similar to the value of 2.074 (1)-2.089 (2) Å in the monoclinic modification[5] or those of 2.078 (2)-2.082 (2) Å in the dithionate salt.[5] With the exception of the O1-Cr-O1′ angle of 79.17 (3)° (vide infra), the angular distortions from octahedral geometry are not severe, with trans angles in the narrow range of 171.77 (4)-172.99 (3)°.

The bridging Cr_2O_2 unit is symmetric, with Cr-O1 and Cr-O1′ separations of 1.974 (1) and 1.972 (1) Å, respectively. These distances are not greatly different from the average values of 1.965 and 1.974 Å in the dithionate and monoclinic chloride structures, respectively.[5]

The Cr-O1-Cr′ bridging angle, ϕ, is 100.83 (3)° in the present case, which is intermediate between the values of 99.92 (3)° for the monoclinic chloride and 101.54 (5)° for the dithionate.[5] As had been predicted by Güdel and co-workers[11,12] on the basis of anticipated hydrogen bonding in the crystals of the cobalt analogue, the hydrogen atom on the bridging hydroxyl group is substantially out of the bridging Cr_2O_2 plane; the deviation in the present case is 0.56 (2) Å, which corresponds to a dihedral angle θ of 50 (3)°. Thus, the θ value here is substantially larger than the value of 24° in the dithionate salt and is probably significantly larger than the value of 41° in the monoclinic chloride. It is noteworthy that, in other bis(μ-hydroxo)chromium(III) complexes, θ values of less than 6° have been reported.[6]

The hydrogen bonding in the crystals is extensive, with all potential donors and acceptors apparently participating. The bridging hydroxo group forms a strong hydrogen bond to a chloride ion, and all of the ammine hydrogen atoms evidently form hydrogen bonds to chloride ions or solvent molecules. The solvent molecules also donate hydrogen bonds to the anions.

The average magnetic susceptibility and effective magnetic moment of a sample prepared by pulverizing two large triclinic crystals of the complex is shown in Figure 2. From the simple Van Vleck Hamiltonian

$$\mathcal{H} = JS_1 \cdot S_2 + g\mu_{\beta MS'}$$

the susceptibility data lead to the values g = 1.985 (3) and J = 1.43 (1) cm^{-1}. Thus, as deduced by Güdel and co-workers from optical spectroscopic measurements,[11,12] the value of J [which corresponds to the triplet energy $E(1)$] is significantly lower then the values of 4.1 and 5.8 cm^{-1} found in the monoclinic isomer and in the dithionate salt, respectively.[5] On the basis of the empirical GHP model,[6] we calculate from the observed values of R, θ, and ϕ a value of 5.89 cm^{-1}. In this parameter range, however, the model predicts that J is extremely sensitive to small changes in θ, the least precisely determined structural parameter, and for the same values of R and ϕ (1.973 Å and 100.83°, respectively) the value of J is calculated as only 1.48 cm^{-1} if θ is increased from 50 to 60°. Such a change in θ is perfectly consistent with the crystallographic results, since it represents an increase of only 3σ in the observed value. Consequently, we must conclude that the observed results are entirely consistent with the model but that conventional X-ray diffraction methods are insufficiently precise in this parameter range to make a thorough test of the model.

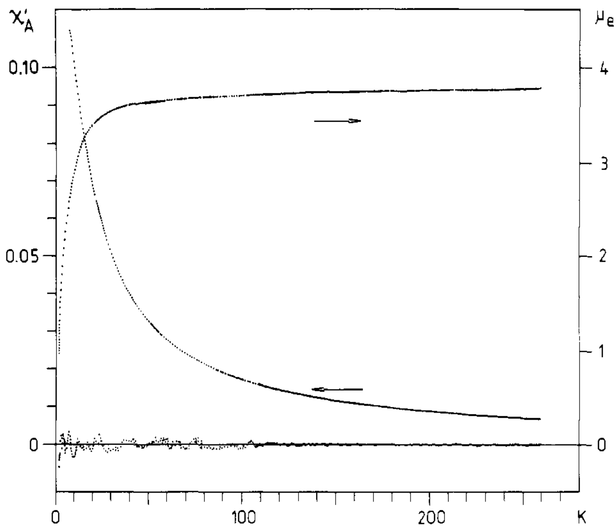

Figure 2. Magnetic susceptibility per chromium (left scale, cgsu) and effective magnetic moment (right scale, μ_B) of triclinic $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$. The lower almost random distribution of dots around the abscissa represents $50(\chi_{obsd} - \chi_{calcd})$ where χ_{calcd} is based on the parameters g = 1.985 and J = 1.43 cm^{-1}.

Acknowledgment. We are very grateful to Solvieg Kallesøe for collection of the magnetic data. This research was supported by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO), through Grant No. 1318 (to D.J.H. and E.P.), by the Petroleum Research Fund, administered by the American Chemical Society (to D.J.H.), and by the Danish Natural Science Research Council through Grants 511-742, 511-3993, and 511-10516 (to E.P.).

Registry No. $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$, 84028-63-7.

Supplementary Material Available: Tables of hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, and observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Preparation of $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$ and $Nb(\eta^5\text{-}C_5Me_5)(3\text{-hexyne})Cl_2$

P. A. Belmonte, F. G. N. Cloke, K. H. Theopold,
and R. R. Schrock*

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We have recently shown that tantalum hydride complexes of the type $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ (R = Me, Et) can be prepared by treating $Ta(\eta^5\text{-}C_5Me_4R)(\text{propylene})Cl_2$ or Ta-